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THE JOURNAL OF THE

TEXTILE INSTITUTE

TRANSACTIONS

1—AN EXPERIMENTAL STUDY OF SHUTTLE PROJECTION

By I. H. THOMAS and J. J. VINCENT

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ABSTRACT.

A method is described for measuring the displacement of the shuttle and the rotation of the loom crank-shaft relative to time and to each other; from these measurements shuttle and loom speeds and accelerations can be derived. It was found that the initial and average shuttle speeds were approximately equal and ranged from 31 to 48 feet per second on the fifteen looms measured. The different speeds produced by different nose-bits were found to be approximately proportional to the nominal displacements after 30 degrees' rotation of the crank-shaft. The shuttle speed was approximately directly proportional to the average loom speed during picking, approximately inversely proportional to the distance of the picking tappet from the picking shaft, and independent of the mass of the shuttle and the position of the buffer. The timing of the pick produced no effect if the sley were stationary, but under normal conditions unsystematic changes occurred, though on the whole a later pick gave a higher shuttle speed. Shortening the picking band and lowering the picking bowl usually increased the shuttle speed. With old picking bands prolonged weaving produced little change, but with new bands the shuttle speed became lower as weaving progressed, partially recovering during rest periods. Measurements of the acceleration of the shuttle showed in a typical instance a maximum deviation of 3·0 inches of the shuttle from its nominal position.* The deviation increased with heavier shuttles and at higher loom speeds. The results were found to agree broadly with theory but there were appreciable detailed discrepancies. Possible causes of these are suggested and a semi-empirical formula for shuttle speed of reasonable accuracy is derived.

INTRODUCTION.

Until recent years no account had been published of accurate observations of the movement of the shuttle in the power loom. The ideas on the subject expounded in text-books and held by overlookers were derived from visual observation (which is necessarily inexact because of the rapid movement of the shuttle and picking mechanism), from inadequate theory, and from mere conjecture. Although the inadequacy of the existing knowledge was expressed as early as 1914 by Woodhouse and Milne[13] there was no development of the subject for many years. Then in 1935 Palmer and Ramsdell[10] described an

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investigation in which a cinematograph was used to record the position of the shuttle and the crank-shaft of an underpick rayon loom at successive instants of time This was followed in 1938 by a paper from Kilgour, Waring and Boffey[6] on experiments with an underpick linen loom in which the movement of the shuttle in the shuttle box was measured relative to that of the crank-shaft by the changes produced in the position of the swell, and relative to time by measuring the movement of a point on the picking stick through the resultant changes of a variable electrical resistance operated by it.

For the investigation described in the present paper a method differing from any of the previous was employed and the motion of the shuttle and the crank-shaft relative to time and relative to each other were determined Measurement of the speed of the crank-shaft was considered a necessary adjunct to the shuttle measurements in view of the demonstrations by Hanton[4] and Honegger[5] of the large cyclic fluctuations that may occur Experiments have been carried out at Lancashire mills, as well as at the Shirley Institute, and although the work has mainly been on overpick Lancashire looms, other types have not been excluded One of the chief objects of the work has been to ascertain what are the effects on the shuttle movement of the usual adjustments made to the picking-mechanism by the overlooker in the course of his duties Another important aim has been to determine how far the theory of shuttle projection published by Vincent,[11] and necessarily based on a simplified view of the loom, applies in practice Also, some attempt has been made to determine forces and dimensions involved in picking with a view to placing loom design on a sound basis.

METHOD AND APPARATUS.

The experimental method consisted in observing the time, measured from an arbitrary origin, and the position of the loom crank, when a specified point on the shuttle coincided with certain points at known distances along the path of the shuttle From this information were obtained the three relations connecting (1) the displacement of the shuttle with time, (2) the displacement of the shuttle with the rotation of the crank-shaft, and (3) the rotation of the crank-shaft with time From these relations were derived the speed and acceleration of the shuttle and the loom at particular instants or averaged over short intervals of time Measurements were made while the shuttle was being accelerated from rest and when it was crossing the race-board, but not when it had entered the shuttle box and was being brought to rest.

Two slightly different forms of the method were employed, depending on whether consecutive points of observation along the path of the shuttle were more or less than about twelve inches apart. Although, as will appear, this differentiation was fixed by the length of the shuttle it also corresponded in the main with the requirements of the two classes of experiments performed In one class the average speed of the shuttle across the race-board was the chief concern and it was usually necessary to take observations only at two points some forty inches or more apart, and in the other class of experiment the shuttle was under observation only while leaving the shuttle box and then the extreme points of observation were ten inches apart

For the race-board measurements the specified point on the shuttle was the centre of a hole half an inch in diameter drilled through the front and back of the shuttle in a direction at right angles to the front wall at a convenient point in its length. The points along the path of the shuttle were at the intersection of this path with the axes of beams of parallel light emitted by galvanometer lamps placed behind the reed and rigidly fixed relative to the loom frame The beams, of circular cross-section, $1\frac{3}{8}$ inch in diameter, were directed at right angles to the swing rail and were placed at such a level that they just grazed the race-board at the back-centre position

Coincidence of the point on the shuttle with one of the specified points on the race-board was indicated by the passage of the beam of light through the hole in the shuttle, and recorded by bringing the light to a focus, after reflection at a plane mirror, on the slit of a recording camera This camera was of the type described by Oxley[8] except that the cylindrical lens was dispensed with The recording paper moved at a speed of 57 cms per second

For the shuttle box experiments, because of the rapid changes in speed, more accurate and more detailed measurements were necessary and therefore observations were made at seventeen points along the path of the shuttle and the speed of the recording paper was increased to 95 cms per second Instead of using seventeen lamps to mark these points, which would have been inconvenient if not impracticable, the equivalent method was adopted of drilling seventeen holes in the shuttle and using one galvanometer lamp. The holes comprised in order one of $\frac{1}{16}$ inch diameter, six of $\frac{1}{8}$ inch, four of $\frac{1}{4}$ inch, and six of $\frac{5}{16}$ inch, and the distances from one centre to the next were respectively $\frac{21}{32}$ inch, $\frac{3}{16}$ inch, $\frac{5}{16}$ inch, seven at $\frac{1}{2}$ inch, and six at one inch The holes were varied in size and spacing to allow for the different speeds at which the different holes passed the beam of light, larger and more widely spaced holes being required as the speed increased in order to render visible and separate the marks on the photographic record In this set of experiments the beam of light was reduced in diameter to $\frac{1}{16}$ inch to give the desired accuracy, and as this size of beam would not be effective if there were any vertical movement of the shuttle it was necessary to disconnect the sley and fix it at the centre of its range of movement for the shuttle acceleration period.*

This change modified slightly the movement of the picker produced by a given picking nose and gave a more uniform loom speed Due account was taken of these effects, but the others produced at the same time—the greater uniformity of the angle of inclination of the picking band to the picker spindle and the absence of forces due to acceleration of the sley—were considered to be negligible

It was essential, if the shuttle box experiments were to be of value, that the starting position of the shuttle and the time at which it started should be accurately known For this reason, projection of the shuttle from a single side was observed (the picking mechanism at the opposite side being rendered inoperative), and before each record was made the shuttle was placed in the shuttle box with the beam of light passing through the first hole of the series Thus the distances moved by the shuttle when each hole was opposite the beam of light were known with sufficient accuracy The slowness with which the shuttle moves at first demands some special method for determining exactly when it starts Accordingly, the initial movement was magnified 4,000 times by inserting between the shuttle and the box front, where it was held by friction, a vertical rod, 3 inches long and $\frac{1}{16}$ inch in diameter, carrying a small plane mirror The rod consisted of a length of catgut This material was used on account of its being sufficiently rigid but with a resistance to bending not large enough to impede the picker if entanglement occurrred, as had been found to happen when a steel rod was employed Light from a galvanometer lamp was reflected from the small mirror and brought to a focus after reflection from a fixed mirror, on the slit of the recording camera Linear movement of the shuttle led to rotation of the mirror and the abrupt interruption of the recorded trace The instant of interruption was taken as the time at which the shuttle started to move When taking a record the loom was started with the picking stick just back again after picking so that nearly two revolutions of the crank-shaft occurred before the recorded pick was delivered, which, as the later records showed, gave the loom ample opportunity, assisted by the absence of motion of the sley, of reaching full speed.

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* The possibility of overcoming the difficulty by using vertical slits, $\frac{1}{16}$-inch wide, cut in the front and back of the shuttle box, was overlooked at the time but has since been used successfully in connection with experiments on checking.

The angular position of the crank-shaft was simultaneously recorded by means of a beam of light from a galvanometer lamp which passed through holes in an aluminium disc, 19⅛ inches in diameter, attached to the hand-wheel and was brought to a focus, after reflection, on the slit of the recording camera. The holes, placed with their centres on a circle 18 inches in diameter concentric with the top shaft, and spaced at angular distances of 18°, were of ¼ inch diameter except for two adjacent ones of diameters ½ inch and ¾ inch. This differentiation allowed the records to be interpreted in terms of the direction of rotation of the top shaft and the angular movement of the crank-shaft from a fixed reference position

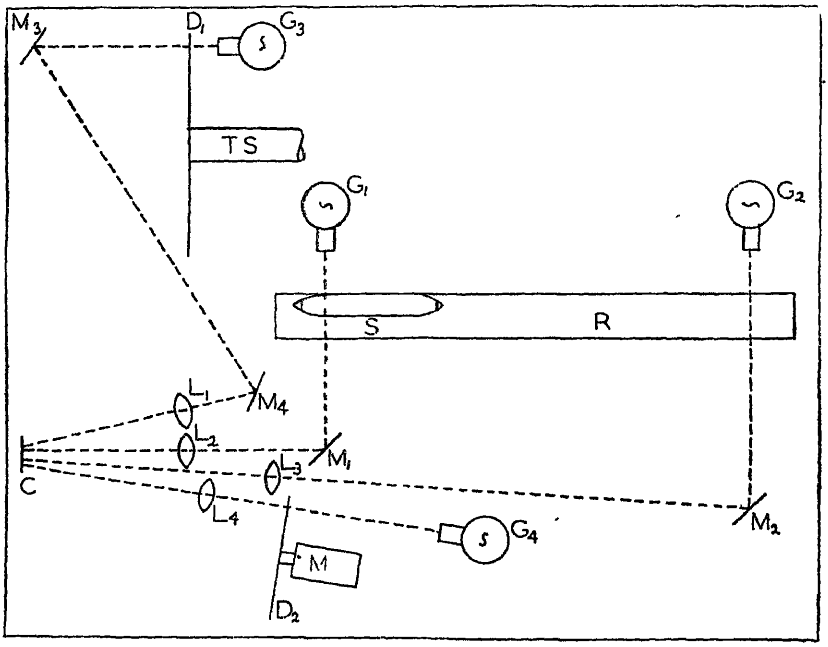
A time-scale was recorded on the same paper by a beam of light, provided by another galvanometer lamp, which was focussed on the slit of the camera and interrupted at regular intervals The interruption was achieved by interposing between the lamp and the camera an aluminium disc provided with uniformly spaced radial slots and concentrically fixed to the spindle of a self-starting synchronous motor of the rotating switch type The number of slots and the speed of the motor were such as to make the distance between consecutive marks on the record correspond to an interval of 0·00136 second, calibration of the motor being effected by means of a cathode ray tube and the public electricity supply of frequency 50 cycles per second.

A plan view of the general arrangement of the apparatus is shown diagrammatically in Figure 1. G_1, G_2, G_3, G_4 ie the four galvanometer lamps employed when observations were taken at two points along the race-board , M_1, M_2, M_3, M_4 are the plane mirrors for directing the beams of light on to the slit C of the camera , L_1, L_2, L_3, L_4 are the convex lenses necessary for focusing the beams , D_1 is the disc on the hand-wheel, D_2 is the disc on the synchronous motor M ; S and R are the shuttle and race-board respectively.

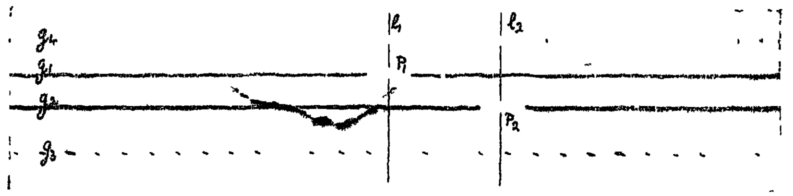
Part of a typical record obtained from race-board measurements is shown in Figure 2. A complete trace usually recorded data relating to seven consecutive picks from which average values were obtained The lines g_1, g_2, g_3, g_4 result from the beams of lamps G_1, G_2, G_3, G_4 respectively The points P_1, P_2 indicate coincidence of the hole in the shuttle with the light from the lamps G_1 and G_2 , the corresponding points on the time and angle scales were obtained by scoring fine lines l_1 and l_2 on the record through the centres of the dots P_1 and P_2 and at right angles to the lines g_1 and g_2 Fractions of the recorded units of time and angle were obtained by microscopic measurement, the linear distances on the record being assumed proportional to the time and angle over the short intervals involved In this way the time and the angular position of the crank-shaft corresponding to P_1 or P_2 were measured to 0·0004 second and 0·5° respectively The corresponding positions along the race-board were obtained by measuring with a ruler the distances from some fixed point of the axes of the beams from lamps G_1, G_2. These distances were determinable to 0·1 inch Thus an average speed of 40 feet per second would be determinable within about ± 0·3 feet per second with the lamps placed 40 inches apart.

A typical record obtained from shuttle box measurements is shown in Figure 3. The lines g_3 and g_4 arise from the lamps G_3 and G_4 as before , the line g_1 arises from the lamp G_1 placed behind the shuttle box, and g_5 is the line resulting from the small mirror used for showing when the shuttle starts to move The records were measured up as before but the higher paper speed enabled time intervals to be measured to 0·00024 second and the crank angle to 0·3° The centre distances between the holes in the shuttle were measured microscopically to 0·003 centimetre Hence a single measurement taken over a distance of one inch would give a speed of 40 feet per second to an accuracy of ± 4·8 feet per second.

(1)



(2)



(3)

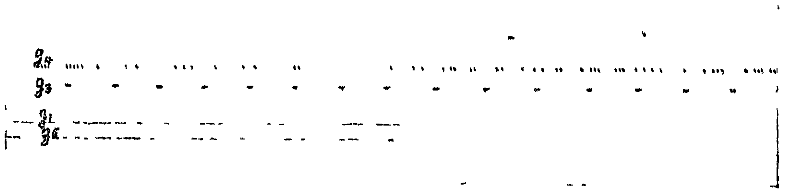


Fig 1 Schematic arrangement of apparatus.

Fig 2. Part of trace obtained from shuttle speed determinations

Fig. 3 Part of trace obtained from shuttle acceleration determinations

To ensure in the race-board experiments that the shuttle started from the same rest position at the beginning of each pick, and thus avoid attributing to the picking any variations that might be caused by the checking, an indicator was fixed to the front of the loom opposite the shuttle box. The indicator consisted of a cylindrical steel rod sliding freely in a steel tube and carrying at its front end a steel needle, its rear end resting on a compression spring inserted in the tube The steel tube was firmly attached to the loom frame in such a way that when the sley was at front centre the needle passed through a hole made in the box front and impinged on a strip of paper fixed to the front of the shuttle. If the shuttle came to rest at the same position at the end of each pick all the marks made on the paper by the needle coincided, but if the running of the shuttle were erratic the marks were spread out, thus giving indication of the fault, which was then remedied

A further measurement that was made on some of the overpick looms was of the vertical deflection of the end of the picking stick relative to its horizontal displacement This relation was obtained directly as a curve by inserting in an axial hole in the free end of the picking stick a spring-seated pencil which drew a line on a sheet of paper attached to a metal plate forming part of a cylinder concentric with the picking shaft

LOOMS INVESTIGATED.

Details of the looms on which experiments were carried out are given in Table I. The looms were without warps, except where stated, but unless some setting had been deliberately altered they were in the same condition as they had been when weaving was in progress Once a setting had been changed, however, the loom was not necessarily altered again provided the setting was within the practical range of variation. Hence the same loom might give considerably different shuttle speeds on different occasions For any particular experiment no change was made, of course, other than that referred to Looms 2, 3, 4, 5, 8, 10, 11 were investigated at the Shirley Institute, the remainder at Lancashire mills.

RESULTS.

(1) Comparison between Initial Shuttle Speed and Average Speed during the Traverse.

A knowledge of the relation between these two speeds is desirable in order to co-ordinate the picking with the shedding It is clear, however, that if the shuttle is pressed between the two sheets of warp during part or all of the traverse, no definite relation between the average and initial speeds can exist, for it is a matter of common experience that in such circumstances the retardation may vary from a negligible amount to one sufficient to arrest the shuttle before completing the traverse Results of general application can be expected only when the shuttle is not seriously impeded by the top shed during the traverse or when the warp is absent In such circumstances it is then clear on theoretical grounds that the average shuttle speed cannot be appreciably less than the initial speed , for, assuming the traverse takes about 1/10th second, a difference of as little as 1 foot per second would require a retarding force of about two-thirds of the weight of the shuttle acting on it over the whole of the traverse This would presuppose a high coefficient of friction between the shuttle and the parts in contact with it, whereas the friction at such a speed of rubbing would be expected to be small [2]

The experimental results accord with this view, and show a difference between the initial and average speeds so small as to be of no practical importance Measurements were made on loom 2, using two holes in the shuttle, 7 inches apart, and two lamps behind the reed, one at each end of the race-board Results are given in Table II for seven consecutive picks made with the warp absent It will be noticed that the shuttle was projected at an appreciably higher speed from one side than from the other. That the average speed is apparently larger than the initial in one instance is the result of experimental errors

Table I

Details of Looms Investigated

Loom No	Maker	Type	Reed space, inches	Drive	Usual speed, P P M
1	——	Cone overpick, fast reed	36	Fast and loose pulleys from overhead shaft	195
2	Butterworth & Dickinson	Cone overpick, loose reed	45	By chain direct from electric motor	201
3	Wm Dickinson	Cone overpick, loose reed, controlled swells	45	By chain direct from electric motor	181
4	Hattersley	Cone overpick, loose reed, circular box	45	By chain direct from electric motor	163
5	Butterworth & Dickinson Shirley Institute	Cone overpick, loose reed, controlled swells	45	By chain direct from electric motor	250
6	Butterworth & Dickinson	Cone overpick, fast reed	45	Fast and loose pulleys from overhead shaft	170
7	Butterworth & Dickinson	Cone overpick, fast reed	45	Fast and loose pulleys from overhead shaft	184
8	Wm Dickinson	Cone overpick, fast reed	45	By chain direct from electric motor	193
9	Hattersley	Cone overpick, loose reed, circular box	60	Fast and loose pulleys from overhead shaft	168
10	Hacking	Cone overpick, fast reed	60	By chain direct from electric motor	171
11	Wm Dickinson	Cone overpick, fast reed	60	By chain direct from electric motor	163
12	Butterworth & Dickinson	Cone overpick, fast reed	60	Fast and loose pulleys from overhead shaft	163
13	Butterworth & Dickinson	Cone overpick, fast reed, 16-shaft dobby, weaving cloth	60	Fast and loose pulleys from overhead shaft	152
14	Butterworth & Dickinson	Cone overpick, fast reed	70	Fast and loose pulleys from overhead shaft	146
15.	Butterworth & Dickinson	Cone overpick, fast reed, sheeting loom	78	Fast and loose pulleys from overhead shaft	138
16	Butterworth & Dickinson	Cone overpick, fast reed, sheeting loom	92	Fast and loose pulleys from overhead shaft	121
17.	Butterworth & Dickinson	Cone overpick, fast reed, sheeting loom	106	Fast and loose pulleys from overhead shaft	117
18	Northrop	Cone underpick, fast reed, automatic bobbin change	40	Fast and loose pulleys from overhead shaft	170
19	Northrop	Cone underpick, fast reed, jacquard, weaving cloth	70	By vee-belt through clutch, from electric motor	135
20.	Northrop	Cone underpick, fast reed, jacquard, weaving cloth	70	By vee-belt through clutch, from electric motor	141
21	Northrop	Cone underpick, fast reed, automatic bobbin change	45	By vee-belt, through clutch, from electric motor	175
22.	Crompton & Knowles	Underpick, fast reed, multiple box, automatic shuttle change	50	By vee-belt through clutch from electric motor	149

Table II

Initial and Average Shuttle Speeds ; Consecutive Picks ; Loom 2, no Warp.

Initial .	40·0	36·5	40·5	36·8	40·1	37·0	40·1	feet per second
Average	40·4	35·6	40·3	35·5	39·6	35·8	39·6	feet per second

Although this result is in agreement with theory, it does not accord with a result given by Palmer,[9] who found a reduction in speed of 12·4% to occur between the time the shuttle attained its maximum speed and the time it reached the nearer selvedge. A comparison with the results of Kilgour, Waring and Boffey[7] is inconclusive on account of the large but unsystematic variation with loom speed of the difference between initial and average shuttle speeds found by those authors, the maximum and minimum differences being 8·4 feet per second and −0·9 feet per second

Similar results were obtained when a cotton warp, containing 104 ends per inch of 32s was present, provided there was no undue pressure of the warp on the shuttle This is shown by Table III, where the pick from one side was timed progressively later, which progressively reduced the clearance between the top shed and the front of the shuttle as it left the shed until interference occurred. The clearance was measured when the rear of the full cross-section of the shuttle had reached the selvedge It will be seen that the interference was quite large before the average speed was seriously reduced.

Table III

Initial and Average Shuttle Speeds ; Loom 2 ; 32s Warp, 104 Ends per inch.

Position of crank relative to bottom centre when picking band was taut	Clearance between top shed and front of shuttle when leaving shed	Speed in feet per second		
		Initial	Average	Difference
54° before	0·4 inch	31·9	30·9	1·0
30° before	0·3 inch	33·6	33·3	0·3
15° before	0·0 inch	35·2	34·4	0·8
6° before	−0·3 inch	36·7	35·7	1·0
10° after	−0·7 inch	38·8	36·6	2·2
22° after	−1·1 inch	39·9	36·6	3·3

The practical equivalence of the initial and average speeds is useful for experimental purposes, because it is possible to measure the average speed more readily than the initial speed, and for this reason only the average speed across the race-board was measured in much of the subsequent work.

(2) Average Shuttle Speeds on Cotton Looms : Typical Values.

Although, as will be seen later, variations in loom settings may alter the shuttle speed appreciably, the typical values in Table IV for looms on routine weaving, as set by the overlookers in charge, are not without interest in view of the paucity of published results derived from direct measurement It is true that many of the estimates obtained indirectly are substantially correct, as, for example, in Hanton's statement[3] that "it is not generally considered desirable to attempt to run at a higher shuttle speed than between 45 and 50 feet per second . but . . . the shuttle speed generally approaches the figure given," but other estimates are very wide of the mark, as, for instance, the speed of 75 feet per second given in the Science Museum Catalogue of Textile Machinery.[1]

It will be seen from the table that on the whole both the shuttle speed and the relative shuttle speed (as the ratio average shuttle speed/average loom speed may conveniently be called) increase with increasing reed space. The evidence, as far as it goes, also supports the expectation that, for a given reed-space, fast-reed looms demand a higher relative shuttle speed than loose-reed looms.

Table IV

Typical Values of Shuttle Speeds for Looms on Routine Weaving (Mean of Picks from both sides).

Loom No	Type of warp protector	Reed space, inches	Loom speed, picks per minute	Shuttle speed, ft per sec	$\frac{\text{Shuttle speed}}{\text{Loom speed}}$
2	Loose reed	45	201	36	0 18
4	,, ,,	45	163	31	0 19
5	,, ,,	45	250	42	0 17
9	,, ,,	60	168	36	0 21
7	Fast reed	45	184	40	0 22
11	,, ,,	60	163	46	0 28
14	,, ,,	70	145	43	0 29
15	,, ,,	78	138	45	0 27
16	,, ,,	92	120	46	0 38
17	,, ,,	106	117	48	0 41
18	,, ,,	40	170	36	0 22
19	,, ,,	70	135	37	0 27
20	,, ,,	70	141	36	0 26
21	,, ,,	45	175	41	0 23
22	,, ,,	50	149	33	0 22

(3) Factors affecting the Initial Shuttle Speed.

Shape of the Picking Tappet.

The primary factor controlling the shuttle speed at a given loom speed is the shape of that part of the picking tappet in contact with the picking bowl while the shuttle is being accelerated, and this may be specified in terms of the relation between the nominal displacement of the shuttle and the rotation of the crank-shaft Such a specification is dependent on other factors such as the dimensions of the connections between the picker and the picking tappet and the movement of the sley, but if these factors are kept constant the specification is valid for comparing different nose-bits.

Loom makers supply nose-bits to give picks of different "strengths," (that is, different shuttle speeds), and these are marked with dots in increasing numbers to indicate higher shuttle speeds, the different nose-bits being employed usually with looms of different widths Although it is unlikely that there is any consistency between the markings of different makers, the shuttle speeds produced by a series of nose-bits from one maker are of interest for the purpose of showing what differences in speed are considered important.

Four different nose-bits supplied by one maker were employed on loom 2. The speed of the shuttle and its nominal displacement relative to the rotation of the crank-shaft were measured in each instance The results are given in Table V.

Table V

Shuttle Speed and Nominal Displacement for different Nose-bits ; Loom 2

Number of dots marked on nose-bit	4*	5	6	7
Shuttle speed, feet per second	41 1	44 1	49 3	59 3
Nominal displacement after 30° rotation of crank-shaft, inches	7 80	8 45	9 70	11 18
Shuttle speed—nominal displacement at 30°	5 27	5 22	5·08	5 30

* Usual nose-bit for this loom

The corresponding curves of the nominal displacement of the shuttle plotted against the crank angle are given in Figure 4. Inspection of the graphs shows that during the phase of picking that theory shows to be important, that is, for any particular value of the crank angle less than about 30°, (Vincent, *loc cit.* p 9), the displacement and the slope of the displacement curve were greater the larger the shuttle speed and the number of dots.

The approximate constancy of the last row of figures in the table shows that the shuttle speed was approximately proportional to the nominal displacement of the shuttle after thirty degrees' rotation of the crank-shaft.

Loom Speed.

Measurements of the cyclic fluctuations in loom speed during each revolution of the crank-shaft showed that the average loom speed during the traverse of the shuttle was not materially different from the average taken over a whole revolution. The results are exhibited in Table VI

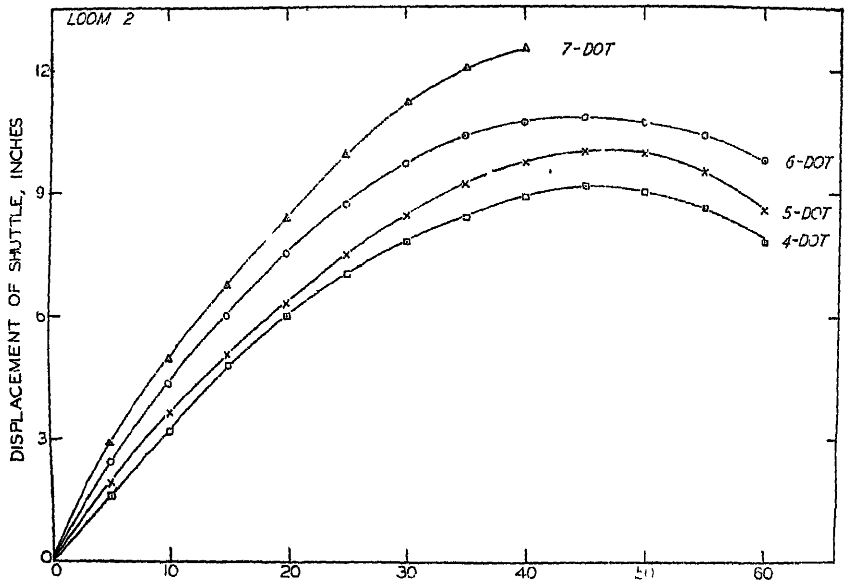


Fig 4.
Nominal movements for different picking noses.

Table VI
Average Loom Speeds over a Complete Revolution and during Traverse of Shuttle

Loom number	2	5	5	10	15	16	20	22	22	22
Average loom speed, picks per minute	201	250	201	171	138	121	141	141	149	159
Average loom speed during shuttle traverse, p p m	200	250	200	169	137	121	143	141	147	158

Now, since the rates of movement of the sheds and the sley are proportional to the loom speed, it follows that it is desirable for the shuttle speed to be proportional to the average loom speed if the same movement of the shuttle relative to the warp is to be obtained at all speeds without adjusting the picking Measurements were made to see how nearly this ideal was approached. In addition, the average loom speed during the shuttle acceleration period was observed, for it is the loom speed during this period that determines the shuttle speed, and a knowledge of its value is necessary when comparing the observed results with theoretical expectations

One series of experiments was carried out on loom 2. When the loom speed was altered no change was made in the loom settings except to adjust the swell pressure so that the shuttle started from the same point in the shuttle box at all speeds. The swell resistance was never large enough, in view of the results of Table XVIII, to produce any appreciable effect on the shuttle speed. In addition, the relation between the shuttle speed and the loom speed during picking was readily obtained for a number of speeds without changing the average loom speed merely by starting the loom with the crank at different positions and measuring the shuttle speed for the first pick and the loom speed while the shuttle was being accelerated. Typical results obtained by both methods are given in Tables VII and VIII.

Table VII

Shuttle Speed at Various Loom Speeds; Loom 2

Average loom speed, picks per minute	171	185	202	216
Average loom speed during shuttle acceleration period, p.p.m.	162	169	188	198
Shuttle speed, feet per second	38.5	39.0	41.6	42.8
Relative shuttle speed	0.225	0.211	0.206	0.198
Shuttle speed—average loom speed during shuttle acceleration period	0.238	0.230	0.221	0.216

Table VIII

Shuttle Speed and Average Loom Speed during Shuttle Acceleration Period; Loom 7

Average loom speed during shuttle acceleration period, p.p.m.	110	123	129	136	145
Shuttle speed, feet per second	28.1	31.1	32.5	34.1	35.5
Shuttle speed—average loom speed during shuttle acceleration period	0.255	0.253	0.252	0.251	0.245

It will be seen that the relative shuttle speed was not constant but increased on loom 2 by 12½ per cent when the loom speed was reduced from 216 to 171 picks per minute, showing that the shuttle speed was not strictly proportional to the loom speed. There was also a change in the ratio of the shuttle speed to the average loom speed during the shuttle acceleration period which is of theoretical interest. Results qualitatively similar to these were found for a number of looms of different widths and various settings.

Timing of the Pick.

For these experiments the timing of the pick was varied over a much wider range than would have been possible had the warp been present. The results in Table IX show that on the whole the tendency was for a later timing to give a higher shuttle speed. The changes in speed with timing were less with the underpick loom than with the overpick looms and were absent with an overpick loom when the sley was fixed. These results can be explained in terms of the geometry of the picking mechanism and the variations in loom speed and will be discussed in more detail in a later section.

Table IX

Variation of the Shuttle Speed with the Timing of the Pick

Loom 2	Timing*	+45	+35	+17	+5	−10	−22
	Shuttle speed, ft. per sec.	27.5	27.8	28.5	29.2	30.7	32.1
Loom 2 short picking band	Timing	+54	+40	+25	+5	−6	−22
	Shuttle speed, ft. per sec.	33.3	32.8	32.2	32.0	32.8	34.5
Loom 5	Timing	+42	+26	+8	−10	—	—
	Shuttle speed, ft. per sec.	39.7	40.8	42.7	44.0	—	—
Loom 21	Timing	+20	+7	−15	−22	—	—
	Shuttle speed, ft. per sec.	40.5	40.7	41.0	41.6	—	—
Loom 2 sley fixed	Timing	+55	+36	+12	−5	−18	—
	Shuttle speed, ft. per sec.	35.7	35.9	35.9	35.6	35.7	—

*Position of crank when picking band was taut measured in degrees before bottom centre.

Length of the Picking Band.

Changing the length of the picking band is one of the simplest and most frequent adjustments that is made to the picking mechanism during routine weaving. It is also a change that may occur spontaneously through stretching (particularly if the band be new), through recovery from stretch when the loom is stopped, and through changes in humidity. Such a change in length produces a double effect: it alters the timing of the pick and also the position of the picking bowl on the nose-bit at the instant when the band is taut. It is possible, though not often done in the course of routine overlooking, to separate the two effects by correcting for the change in timing by altering the angular position of the picking tappet on the bottom shaft, which leaves unchanged the position of the bowl on the nose-bit at which the picking band becomes taut.

The omnibus effect produced by changing the length of the band and making no other alterations was observed on a number of looms, and except in one instance, where the speed reached a maximum and then decreased, progressive shortening of the band led to a marked progressive increase in shuttle speed. Typical results are given in the second and fourth lines of Table X, and the exception is given in the sixth line.

Table X

Variation of Shuttle Speed with Length of Picking Band

Loom 2	Length of picking band, inches*	17·8	18·1	19·4	20·8	22·0
	Shuttle speed, ft per sec	46·3	45·2	41·1	37·5	31·9
Loom 7	Length of picking band, inches†	9·8	10·7	11·5	12·7	—
	Shuttle speed, ft per sec	41·7	39·8	35·4	28·8	—
Loom 17	Length of picking band, inches‡	11·0	11·3	12·1	13·1	13·6
	Shuttle speed, ft per sec	51·7	52·6	53·6	50·2	49·8

*Measured from picker to first pin on stick, usual length 19·4 inches.
†Measured from picker to end of stick, usual length 10·7 inches
‡Measured from picker to end of stick, usual length 11·0 inches

By itself, the change in length of the band produced little change in shuttle speed as was shown by another experiment on loom 2 in which the other effects were nullified by changing the angular position of the picking stick relative to the picking shaft. The results are in Table XI.

Table XI

Effect on Shuttle Speed of Change in Length of the Picking Band but with Timing and Nominal Movement unaltered

Length of picking band, inches*	9·2	9·9	10·5	11·6	12·0
Shuttle speed, feet per second	34·3	34·8	35·3	36·1	36·6

*Measured from picker to end of stick, usual length 10·5 inches

How much of the omnibus effect is produced by the change in timing can be judged, in conjunction with results of the previous section, from the fact that a change of one inch in the length of the band produces a change in timing of four degrees.

It will be seen that the effect is small, and since the length of the band by itself produces little effect, it follows that the major part of the omnibus effect is due to the fact that with different lengths of band the picking bowl is in contact with different portions of the nose-bit at the instant when the band is taut; how the observed facts follow from this is explained in the theoretical section.

Swell Resistance.

Changes in swell resistance may affect the shuttle speed in two ways. There is a direct effect resulting from changes in the resistance offered to the shuttle during acceleration, and there may be an indirect effect, if the swell pressure is great enough, resulting from variation in the position at which the shuttle comes to rest after the previous pick, since variation of the starting position modifies the nominal movement during picking. It is with the direct effect that this section is concerned, and this effect was isolated by measuring the speed for single picks with the shuttle initially at the same position in the shuttle box The swell resistance was measured by attaching one end of a spring-balance to the forward end of the shuttle, placed in the shuttle-box at its normal starting position, pulling on the other end of the balance along the line of the shuttle path until the shuttle moved slowly out of the box, and observing the maximum force recorded. The resistance was variable and decreased rapidly after the shuttle had moved a few inches. The value of the crank angle when the shuttle began to enter the shed was also measured. The results are given in Table XII.

Table XII

Relation between Shuttle Speed and Swell Resistance ; Loom 2
(usual swell resistance 4 5 lb. wt.)

Maximum swell resistance, lb wt .	0 5	2 0	4 5	6 2	7 2
Shuttle speed, feet per second	40 9	41 5	41 8	42 0	42 0
Crank angle* when mid-point of shuttle was 4 2 inches inside edge of reed, degrees	104	104	104	104	10

*Front centre = 0°

It will be seen that the swell resistance, paradoxical though it may appear, increases the shuttle speed to a small extent, but has no appreciable effect on the timing. The explanation is that the picking mechanism is placed under strain by the swell resistance, and when this strain diminishes suddenly there remains an unbalanced force which is available for accelerating the shuttle. Attention was drawn to this effect by Woodhouse and Milne[13] when attempting to account for the difference between the nominal and actual shuttle speeds.

Mass of the Shuttle.

The amount of checking a shuttle requires is dependent on its momentum, that is, on its mass and its speed. Visual observation of the effect of the checking on the shuttle may therefore lead to erroneous views if a reduction in momentum is attributed to a reduction in speed when a reduction in mass is the real cause. For example, the view is often held that under equal conditions a light shuttle moves more slowly than a heavy one. That this view is mistaken is shown by Tables XIII and XIV, where it is seen that the shuttle speed was substantially independent of the mass of the shuttle. Table XIII also shows that the timing was not affected to any important extent, though the tendency was for a heavier shuttle to be picked later. On each loom the external dimensions of the shuttle were kept the same throughout the experiments and the mass was altered by varying the internal fittings. The speed was measured for one direction of traverse only

Table XIII

Relation between Shuttle Speed and Mass of Shuttle ; Loom 5

Mass of shuttle, ounces	Shuttle speed, ft per sec	Crank angle* when mid-point of shuttle passes fixed points in traverse		Crank angle interval for traverse
		On side	Off side	
5 06	41 9	142°	252°	110°
7 06	41 6	143°	253°	110°
8 10	41 5	143°	254°	111°
9 00	41 4	144°	257°	113°

*Front centre = 0°

Table XIV
Relation between Shuttle Speed and Mass of Shuttle ; Loom 22 ; three speeds

Mass of shuttle, ounces	Shuttle speed, feet per second		
	141 picks per minute	149 picks per minute	159 picks per minute
13·5	31·7	33·3	35·5
15·1	31·8	33·2	35·0
18·7	31·7	33·3	34·5

Height of the Picking Bowl.

For all the looms tested the effect of raising the picking bowl within the limits set by the makers (from ½ inch to 1½ inches) was to reduce the shuttle speed. Typical results are given in Table XV.

Table XV
Relation between Shuttle Speed and Height of Picking Bowl

Loom 2	Height of axis of picking bowl above floor, inches	16·1	16·3	16·5	16·8
	Shuttle speed, feet per second . .	35·4	33·6	31·0	30·2
Loom 7	Height of axis of picking bowl above floor, inches	11·7	12·0	12·2	12·5
	Shuttle speed, feet per second	45·6	42·2	38·0	36·9

Distance of the Picking Tappet from the Picking Shaft.

It is obvious that for a given increment in the radius of the picking tappet at its point of contact with the picking bowl there will be a larger increase in angular movement of the picking shaft when the picking tappet is nearer to it than when the picking tappet is further away. For this reason an increased shuttle speed would be expected as the picking tappet was moved nearer to the picking shaft Such a result was found with all the looms tested in this respect, and the figures for loom 2 given in Table XVI may be taken as typical The approximate constancy of the product in the third row shows that the shuttle speed was roughly inversely proportional to the distance of the picking tappet from the picking shaft.

Table XVI
Relation between Shuttle Speed and Distance of Picking Tappet from Picking Shaft ; Loom 2

Distance between central plane of picking tappet and axis of picking shaft, inches .	4·0	4·5	5·0	5·4
Shuttle speed, feet per second ..	39·0	36·7	33·3	31·1
Distance × shuttle speed .	156	165	166	168

Position of the Buffer

The view is held by some that if the picking mechanism is checked immediately after the picking tappet has ceased to exercise control the " pick will be choked " or " strangled " and the shuttle speed will be reduced. This view was not borne out by experiment. The picking mechanism was checked progressively more rapidly by moving the buffer further away from the spindle stud The results are given in Table XVII

Table XVII
Relation between the Shuttle Speed and the Position of the Buffer ; Loom 2

Distance between buffer and picker at end of nominal stroke, inches	0·3	0·9	1·4	1·8
Shuttle speed, feet per second .	43·8	43·8	43·5	43·8

Table XVIII

Changes in Shuttle Speed with Time ; New Brown Hairy Picking Band ; Loom 2

Picks woven	Shuttle speed f p s		Picks woven	Shuttle speed f p s		Picks woven	Shuttle speed f p s		Picks woven	Shuttle speed f p s
0	39 7	Loom stopped 16½ hours	0	38 3	Loom stopped ½ hour	0	36 6	Loom stopped 16½ hours	0	37·7
6,300	37 9		6,700	37 0		9,700	36·1		11,500	36 7
14,100	37 2		21,500	36 0		24,700	35 9		—	—
26,900	36 4		32,300	35 8		41,400	35 8		—	—
33,500	36 0		44,100	35 4		—	—		—	—

Table XIX

Changes in Length of a New Brown *Hairy Picking* Band ; Loom 2

Picks woven	0	83,000	Loom stopped 41 hours	0	36,000	Loom stopped 2½ hours	0	33,000	Loom stopped 17 hours	0	32,000	Loom stopped 3 hours	0
Length of band, ins	30 3	31 8		31 4	31 9		31 6	32 0		31 7	31 9		31 7

Table XX

Changes in Shuttle Speed with Time ; On-side and Off-side Bands previously used for 7 9 and 2 4 million Picks, respectively ; Loom 2

Picks woven	0	17,600	31,900	41,500	Loom stopped 16½ hours	0	12,000	25,100	34,200	47,500
Shuttle speed, f p s — On to off .	40 1	41 3	41 5	41 5		41 2	41 6	41 6	41 6	41 6
Shuttle speed, f p s — Off to on .	42 7	43 4	43 0	43 0		43 0	43 2	43 5	43 5	43·5

Prolonged Weaving.

It is clearly desirable that there should be no spontaneous changes in the shuttle speed as weaving continues. Such changes may arise through the working loose of nuts and bolts, through changes in length of the picking bands, and through changes in the degree of checking. None of these causes operates in a sufficiently systematic way for profitable study with the exception of the change in length of the picking bands. It is well known that new picking bands stretch, and this, by the results of an earlier section, will lead to a lowering of the shuttle speed. Measurements show, however, that the stretching process is not continuous ; the bands recover partially from the stretching when the loom is stopped and there is a corresponding increase in shuttle speed on re-starting These results are given in Tables XVIII and XIX.

After some time the changes in length and the resultant changes in shuttle speed come to an end. It is not possible to state generally when this will occur, but the period is of the order of half a million picks . When old picking bands were used the changes in speed were small and irregular as shown in Table XX These results also suggest that where the humidity and the temperature are maintained constant the effects of other disturbances are small.

Initial Gap between Picker and Shuttle

From time to time in the course of routine weaving the shuttle may be obstructed in its passage through the shed, and may come to rest in the shuttle box with a space between it and the picker. As a result, the shuttle speed may be so reduced on the next pick that a bang-off or shuttle trap results It is of interest therefore to investigate the relation between the gap and the falling off of shuttle speed. This was done for a conventional picking nose and for one giving a constant nominal acceleration (Vincent, *loc. cit.* p. 9) Single picks were measured, the loom being started from rest with the shuttle at the desired distance from the picker. The results are given in Table XXI.

Table XXI

Effect on Shuttle Speed of Initial Gap between Picker and Shuttle ; Loom 2

Initial gap between shuttle and picker, inches		0·0	1·0	2·0	3·0	4·0	5·0
Shuttle speed, f p s	Conventional picking nose-bit	37·0	34·0	30·6	28·5	26·5	24·4
	Constant nominal acceleration nose-bit	37·0	35·9	34·6	33·1	31·2	28·7

With the standard nose-bit the falling off in speed begins to be serious when the initial gap exceeds one inch, but a similar stage is not reached with the constant nominal acceleration nose-bit until the gap exceeds two inches For all values of the initial gap the latter nose-bit gives a greater speed. This property would lead to more reliable running during routine weaving than is given by the standard nose-bit

(4) The Acceleration of the Shuttle

Of less interest to the overlooker, but of great importance to the loom designer, is the way in which the initial shuttle speed is built up, for on this depends the magnitude of the maximum force required for picking which in turn determines the necessary strength of the parts of the mechanism concerned. The distance travelled by the shuttle while being accelerated is also of interest because it shows whether or not the shuttle boxes are being used to the best advantage.

The sley was kept fixed for all the experiments described in this section This was done in order to reduce the fluctuations in the speed of the bottom shaft and in the height of the shuttle above floor-level, so easing the experimental difficulties. Nevertheless, the broad conclusions reached apply to similar looms with the sley oscillating in the usual way.

A typical displacement/time curve from loom 2 is shown in Figure 5 (curve 2), together with the nominal displacement/time curve (curve 1) obtained by turning the loom over by hand, noting the successive positions of the shuttle and the corresponding values of the crank angle, and finding the equivalent instants of time from a knowledge of the average loom speed during picking. The nominal displacement/time curve obtained in this way is slightly inaccurate owing to the change in loom speed during picking, but as the sley was fixed this change in speed was only about 2 per cent., and the error in the nominal curve is correspondingly small. Also shown in Figure 5 are the curves of the difference between the actual and nominal displacements, of the speed, and of the acceleration. The last two curves were derived by drawing a smooth curve through the points obtained by plotting the actual displacement against time, measuring the slope of the curve at intervals, plotting the values of speed thus obtained, drawing a smooth curve through them, and then repeating the process to obtain the acceleration curve. The accuracy of this last curve cannot be very high, and the large apparent acceleration initially may be due in part to cumulative errors. Similar remarks apply to Figure 11.

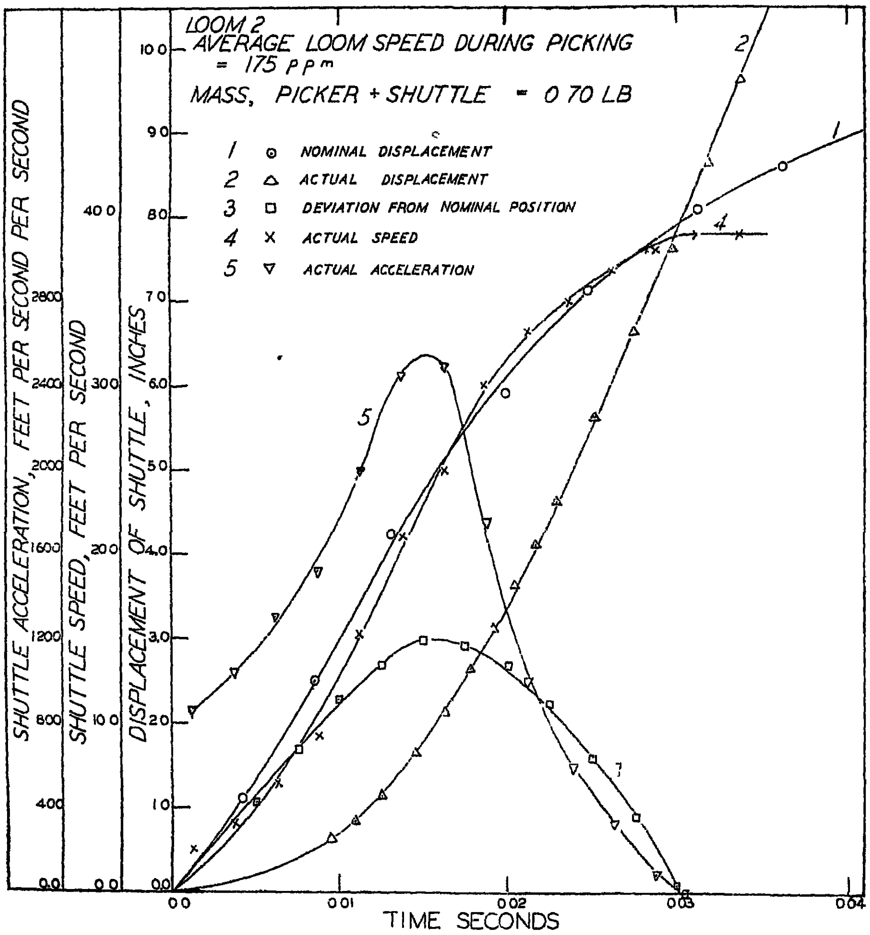


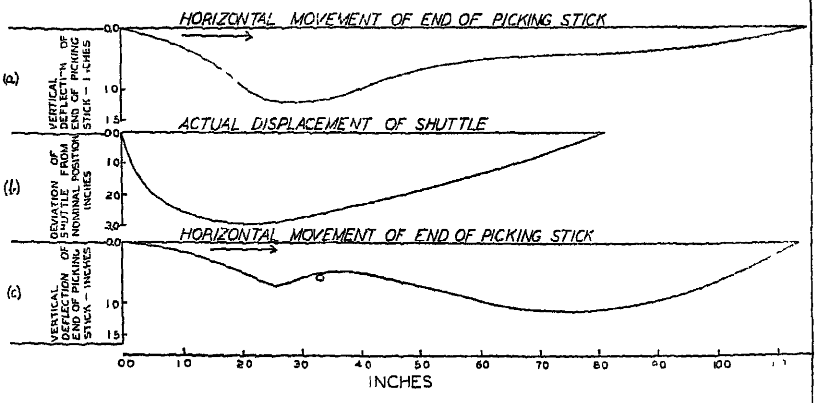
Fig 5

Displacement, speed and acceleration of the shuttle during picking for the conventional type of picking nose.

Reference to curve 3 of Fig 5 shows that the actual and nominal positions of the shuttle coincided initially, reached a maximum separation of 3·0 inches after 0·0155 second, and coincided again after 0·0305 second at which time the maximum shuttle speed of 39 feet per second was attained. Such a deviation of the shuttle from its nominal position corresponds to a force of 60 pounds weight acting on the shuttle and picker with a consequent acceleration of 2,760 ft. per sec. per sec., if the mass of the picking mechanism and the friction at the picker spindle be neglected This is a little more than the maximum observed acceleration, and this fact, in conjunction with the difference in shape of curves 3 and 5, shows that, except near the start, the actual acceleration was always less than would be expected from the force brought into play by the displacement of the picker from its normal position.

Attention may be drawn to the wide fluctuation in the acceleration—from zero to 85 times the acceleration due to gravity—to the smallness of the distance of 1·9 inches moved by the shuttle when the maximum acceleration was reached, and to the fact that the acceleration was completed within a distance of 8·0 inches.

A concrete illustration of the lagging behind and the subsequent catching up of the actual position of the shuttle compared with its nominal position is afforded by the deflection of the end of the picking stick during picking. The curve of the vertical component of the deflection plotted against distance moved horizontally was obtained in the way already described. This curve, shown in Fig. 6 (*a*), is comparable in form with that shown in Fig. 6 (*b*) obtained by plotting the difference between the actual and nominal positions of the shuttle at any instant against the distance moved by the shuttle No exact proportionality can be expected because of the stretching of the picking band and the tendency of the free oscillation of the stick to assert itself as is shown more clearly in Fig. 6 (*c*) at the point O This trace was taken on a similar loom on another occasion.



(a) AND (c) VERTICAL DEFLECTION OF END OF PICKING STICK PLOTTED AGAINST ITS HORIZONTAL MOVEMENT

(b) DEVIATION OF SHUTTLE FROM ITS NOMINAL POSITION PLOTTED AGAINST ITS ACTUAL DISPLACEMENT THE FORM OF THIS CURVE MAY BE COMPARED WITH THOSE OF (a) AND (c)

Fig. 6.

On referring again to Fig. 5 it will be noticed that the shuttle travelled slowly at first, covering, during 25 per cent. of the acceleration time, only 5 per cent. of the total distance over which it was accelerated, and reaching 22 per cent. of its final speed The speed gradually increased, but even when 50 per cent. of the acceleration time had elapsed and the shuttle had reached 59 per cent. of its final speed the shuttle had completed only 23 per cent of its accelerated travel. The nominal speed, as indicated by the slope of curve 1, had a maximum value of 29·2 feet per second. Thus the final actual speed attained was about 1·3 times the maximum nominal speed.

The effect of the mass of the shuttle on the acceleration is shown in Fig 7, which consists of displacement/time curves for three different values of the combined mass of the shuttle and picker, together with the nominal displacement/time curve It will be seen that although the final speed is substantially the same for each mass, as indicated by the slopes of the curves where they intersect the nominal curve, the time at which this maximum speed is reached is greater the larger the mass, as is also the maximum deviation between the actual and nominal positions of the shuttle.

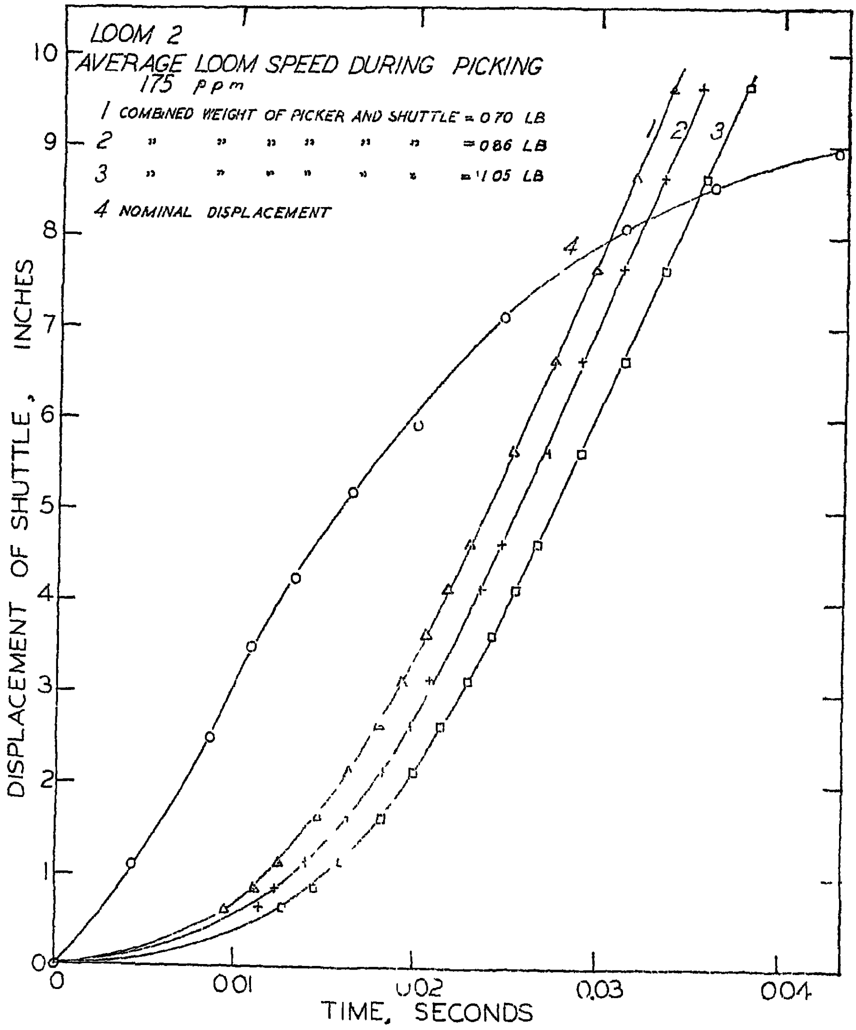


Fig 7

Relation between the actual displacement of the shuttle during picking and the mass of the shuttle

The effect of the speed of the loom on the acceleration of the shuttle can be seen from the curves of actual and nominal displacement plotted against time in Fig. 8 for three different loom speeds and against crank angle in

Fig. 9 for the same three speeds and an additional one. The same nominal displacements appear in all four nominal curves That with a crank-angle base will of course, be the same at all loom speeds, and the others will have the same ordinates plotted against abscissae on different scales With an increase in loom speed the maximum shuttle speed is attained in less time but at a later position in the crank cycle, and with a greater maximum displacement of the shuttle from its nominal position.

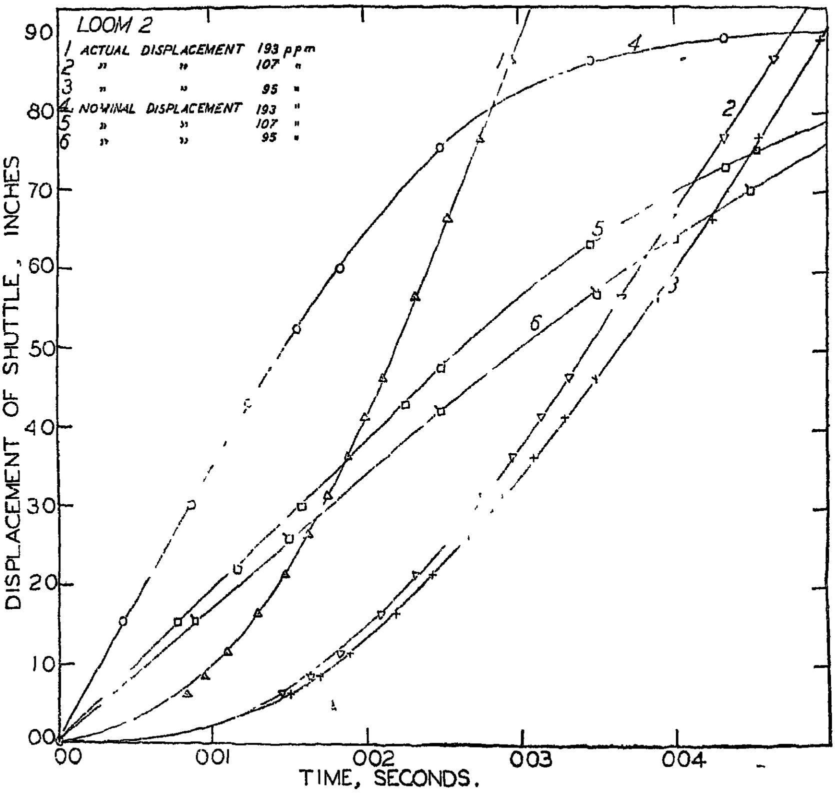


Fig 8

Relation between the displacement of the shuttle and time during picking for three loom speeds

The effect of changes in the equivalent elastic constant of the picking mechanism, denoted by λ, is shown in Fig. 10. To obtain curve 3 the standard picking mechanism was employed, and its stiffness, as measured by the force parallel to the picker spindle required to deflect the picker, was 250 pounds weight per foot. For curve 2 the picking band was replaced by a double length of rubber tubing which gave a value of λ of 80 pounds weight per foot. The maximum shuttle speed attained, as indicated by the final slope of curves 2 and 3, was roughly the same, namely 23 feet per second, for both stiffnesses, but the times taken over attaining it were very different, namely 0.0395 second for curve 3 and 0.0645 second for curve 2. There was also a large difference between the maximum deviation from the nominal position, that for curve 3 being 2.5 inches corresponding to a force of 52 pounds weight, and that for curve 2 being 4.7 inches corresponding to a force of 31 pounds weight Thus by using a more extensible picking band and spreading the acceleration over a larger distance—9.15 inches against 7.45 inches—the same shuttle speed was attained with the expenditure of a smaller maximum force.

All the foregoing experiments on shuttle acceleration were performed with picking nose-bits of the conventional type which give a maximum nominal shuttle speed at or near the start of the pick. The results plotted in Fig. 11 were obtained with a special nose-bit, which, until near the end, gave a constant nominal acceleration from rest. As the shuttle speed was 38.8 feet per second and the combined mass of shuttle and picker 0.7 pound, the results are comparable with those of Fig. 5. In contrast to them the maximum deviation of the shuttle from its nominal position was 2.15 inches against 3.0 inches, corresponding to forces of 43 pounds weight and 60 pounds weight respectively, the maximum acceleration was 1,480 ft. per sec. per sec. against 2,500 ft. per sec. per sec.; and the acceleration extended over 9.8 inches as against 7.9 inches

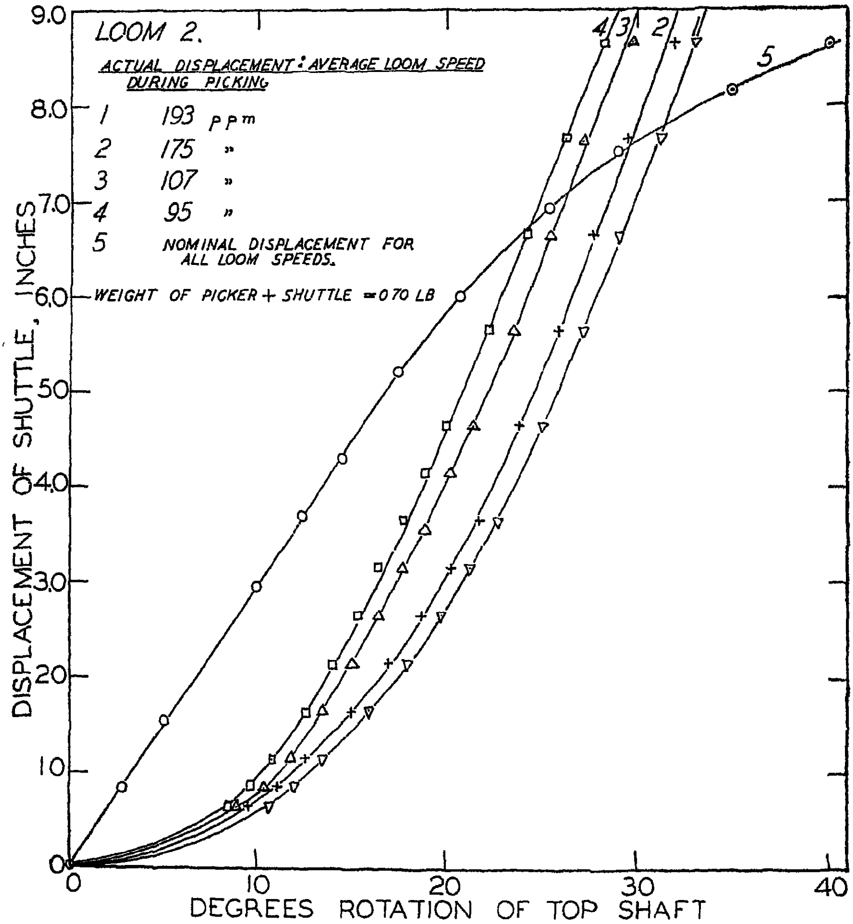


Fig 9
Relation between the actual displacement of the shuttle and crank angle during picking for several loom speeds

DISCUSSION OF RESULTS

Vincent[11] has shown how to calculate the initial shuttle speed in terms of the nominal movement of the shuttle, the loom speed during picking, the effective mass of the picker and shuttle and the stiffness of the picking mechanism. Using the formulæ given in that paper, the shuttle speed has been calculated in a number of instances and compared with the observed speeds. The results are given in Table XXII, together with the ratio of the calculated speed to the observed speed. With one exception the observed speed was less than the calculated.

No reason can be suggested for the exception other than the possibility of an error. For the entries under " loom 2, special nose-bit," loom 2 was fitted with a nose-bit giving a constant nominal acceleration. Loom 22 had a nose-bit giving a relation between the nominal displacement (s) and the crank angle (θ) of the form $s = v\,\theta + q\,\theta^2 + u\,\theta^3$ where u, $\overset{\circ}{v}$ and q are constants. The discrepancies may in part be due to the mass of the picking mechanism and the analogy worked out by Howell[12] suggests that a lowering of the maximum speed could result. That this is not a complete explanation, however, is shown by the results of Table VII, which demonstrate that the shuttle speed is not proportional to the loom speed during picking as it should be theoretically even when the mass of the picking mechanism is taken into account. Other possible sources of discrepancy are the imperfect elasticity of the picking band and, in those instances where the nominal speed is not constant, ignorance of the coefficient of friction between the picker and the spindle for the purpose of determining the effective mass of the picker and shuttle.

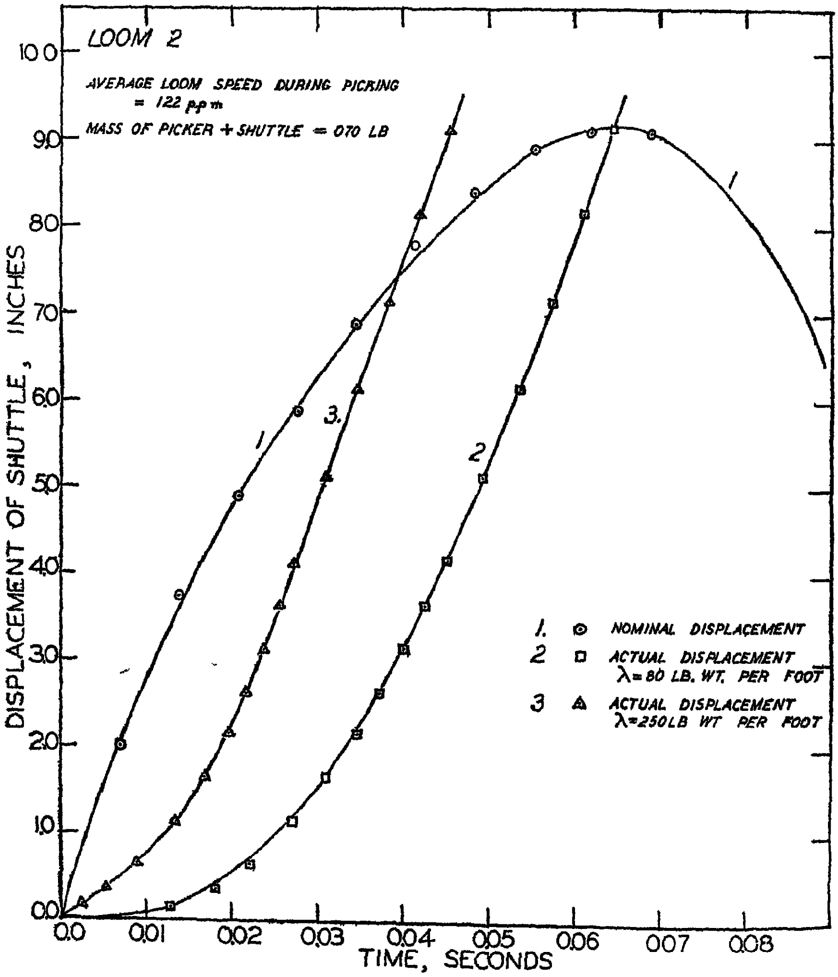


Fig. 10
Effect of the elasticity of the picking mechanism on the actual displacement of the shuttle during picking.

Table XXII

Comparison between Calculated and Observed Shuttle Speeds

Loom number	2				3	7	5	15	16
Observed shuttle speed, feet per second	29 0	35·9	38·5	40·4	33·7	40·7	44·3	43·3	44·4
Calculated shuttle speed, feet per second	36·0	44·6	47·3	48·8	42·5	42·8	51·5	46·4	49·0
Calculated shuttle speed ÷ Observed speed	1·24	1·24	1·23	1·21	1·26	1·05	1·16	1·08	1·10

Loom number :	2 special nose-bit		22			
Observed shuttle speed, feet per second ...	38·8	33·6	29·3	32·4	32·9	33·5
Calculated shuttle speed, feet per second ...	39·4	34·1	27·6	34·2	34·9	35·3
Calculated shuttle speed ÷ Observed speed . .	1·015	1·014	0 94	1·06	1·06	1 05

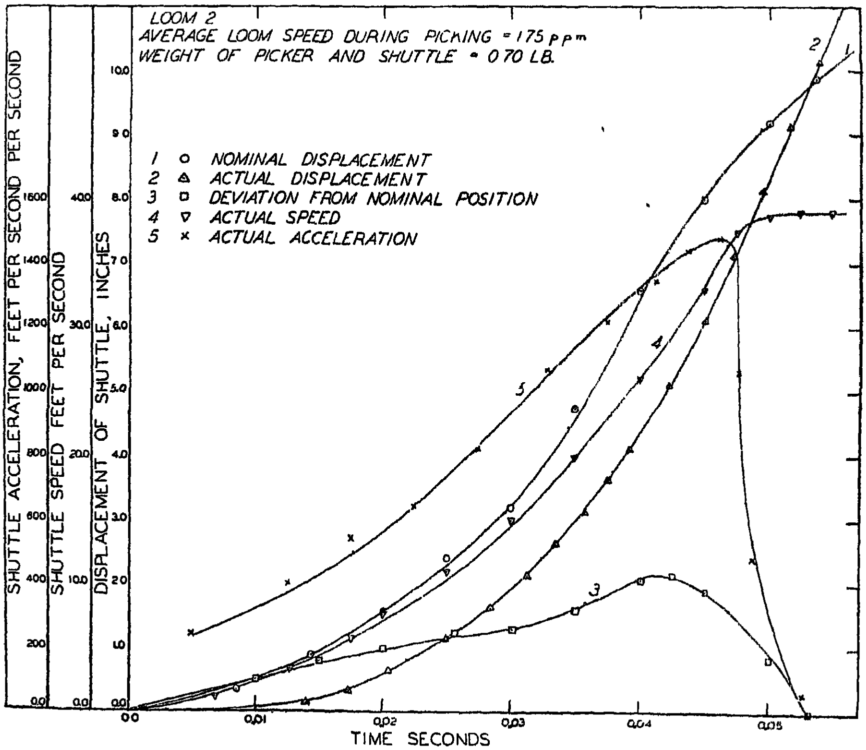


Fig. 11

Displacement, speed and acceleration of the shuttle during picking plotted against time for a constant acceleration picking nose.

The nature of the deviation of the actual displacement of the shuttle from the calculated displacement during the acceleration period is shown in Fig. 12. Curves 1, 2, and 3 are typical of a cone overpick loom with a conventional picking nose-bit. The divergence between the calculated and observed displacements is apparent from the start. With curves 4, 5 and 6 for the constant acceleration nose-bit the divergence between the calculated and observed displacements is only apparent after nearly half the acceleration time has elapsed, though finally the deviations are not much less than with a conventional nose-bit in spite of the smaller discrepancy in respect of the final speed.

At the present stage the cause of the discrepancy between theory and experiment must remain an open question, and the elucidation of it and the replacement of the present theory by a more exact one must wait upon further experiment under simplified conditions with a more homogeneous elastic system than one constructed of leather and wood.

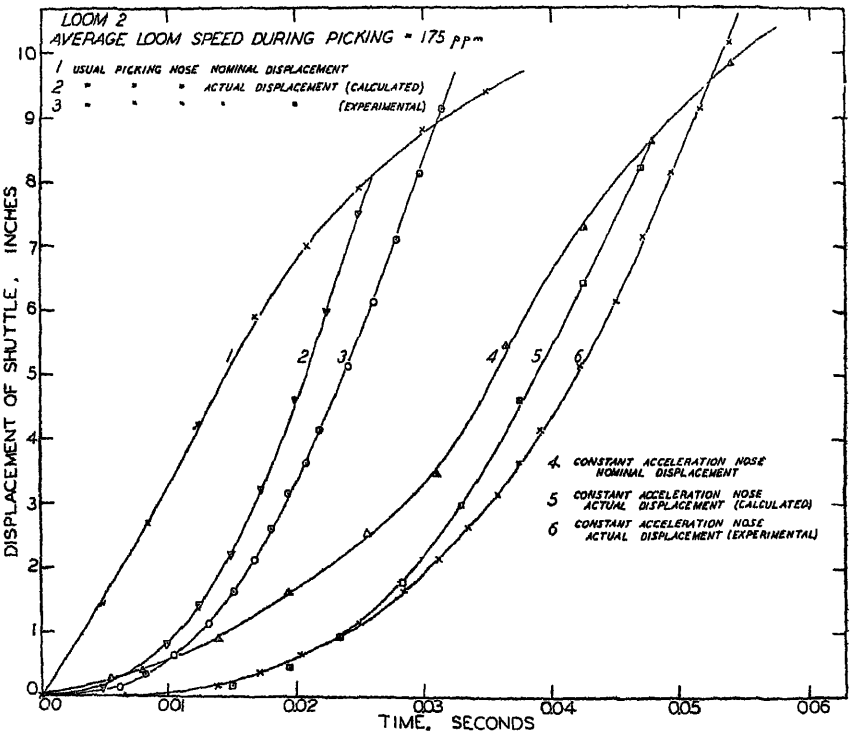


Fig. 12
Curves giving the calculated and experimental values of the displacement of the shuttle during picking for two picking noses

The every-day practical use of the formulæ is hampered by the lack of exact knowledge of the average loom speed during picking in any particular instance, but the difficulty can be partially overcome by using a rough rule derived from a large number of measurements, namely, that the ratio of the average loom speed during picking to the average loom speed is about 0.85 for looms driven by a belt from overhead shafting through fast and loose pulleys, and about 0.92 when driven by a chain direct from an electric motor. Using this and the fact, which follows from Table XXII, that the average value of the ratio of calculated to observed shuttle speeds is about 1.1, the following semi-empirical formula for the initial shuttle speed on Lancashire looms can be given, namely $V = MP/F$, where V = initial shuttle speed in feet per second, M = the distance, in inches, moved by the picker when the loom has turned through 30 degrees from the band-taut position, P = loom speed in picks per minute, and F is the loom factor, which is 39 for a loom driven by a belt through fast and loose pulleys and 36 for a loom driven by chain directly from an electric motor. In Table XXIII comparisons are made for a number of looms between the observed speed and that given by the semi-empirical formula. It will be seen that 60 per cent. of the calculated results lie within ± 5 per cent of the observed and the remainder lie within ± 10 per cent.

Table XXIII

Comparison between Observed Shuttle Speed and that given by the Formula, $V = MP/F$

Loom number:	2	2	5	3	4	8	7	15	16	17
Observed shuttle speed	44·1	41·1	44·3	33·7	33·4	44·4	40·7	43·3	44·4	47·0
Calculated shuttle speed	47·4	43·6	46·0	37·2	34·4	46·1	37·0	42·6	45·3	48·0

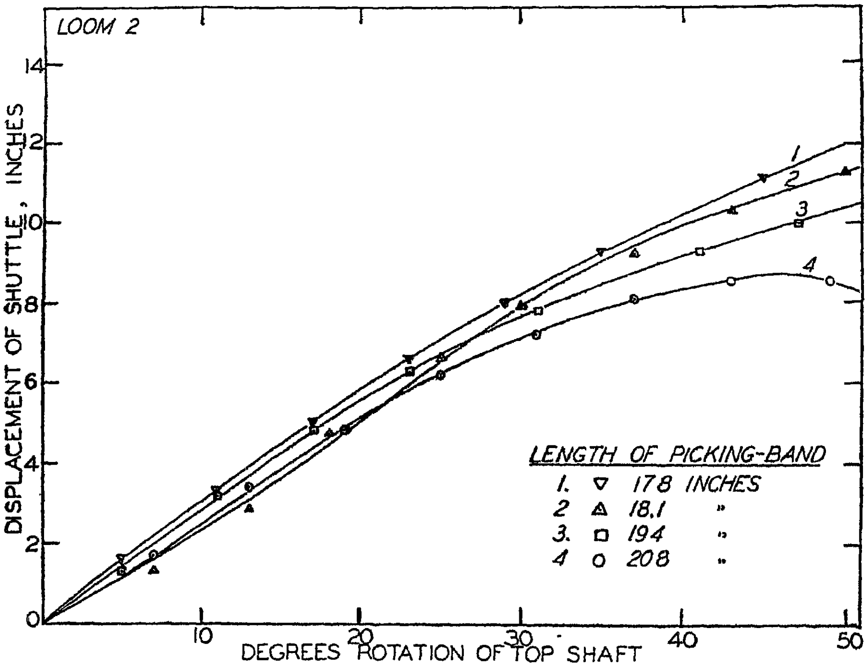


Fig. 13

Nominal displacement curves for various lengths of picking band.

Tables XXII and XXIII indicate that fair agreement exists between the observed and calculated speeds and thus we may assume that the theoretical premises are substantially correct, that is, the shuttle speed is determined in general by the nominal movement, loom speed during picking, the effective mass of the shuttle and picker, and the elasticity of the picking mechanism. Hence changes in shuttle speed produced by changes in loom settings must ultimately be represented by changes in one or more of the above quantities. Thus, in the experiments described in this paper, the effects produced by the shape of the picking tappet, the length of the picking band, the height of the bowl and the distance between the picking tappet and the picking shaft all follow from the different nominal movements they produce, the differences between the average loom speed during picking and the elasticities of the mechanism for the different settings being negligible. A typical set of nominal movements for varying lengths of picking band is given in Fig. 13, the corresponding observed and calculated (using the semi-empirical formula) shuttle speeds being given in Table XXIV.

Thus the changes in the calculated shuttle speed follow those in the observed speed.

Table XXIV

Length of Picking Band, Observed and Calculated Shuttle Speeds; Loom 2

Length of picking band in inches	17·8	18·1	19·4	20·8
Observed shuttle speed in feet per second	46·3	45·2	41·1	37·5
Calculated shuttle speed in feet per second ...	46·0	44·2	42·5	39·5

In Fig. 14 the nominal movements for two positions of the picking bowl are given, the corresponding observed and calculated shuttle speeds being given in Table XXV.

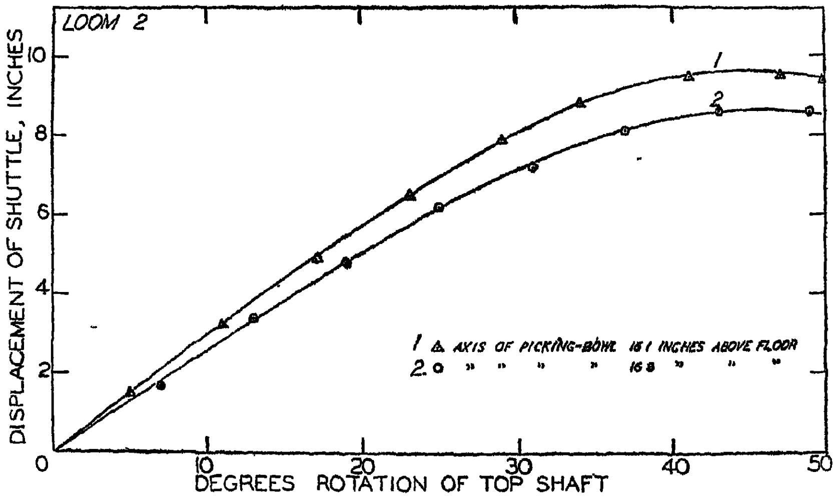


Fig. 14

Nominal displacement curves for two positions of the picking bowl.

Table XXV

Height of Picking Bowl, Observed and Calculated Shuttle Speeds; Loom 2

Distance between the axis of the bowl and floor in inches ..	16·1	16·8
Observed shuttle speed in feet per second	45·4	42·4
Calculated shuttle speed in feet per second	43·0	39·8

Again the changes in the observed speeds are reproduced in the calculated ones.

The effect produced by changes in the timing of the pick follows from the variation in loom speed during picking together with the variation in the nominal movement produced by the movement of the sley. The latter effect is treated analytically in the Appendix. Fig. 15 gives the nominal movement for three timings of the pick for loom 17, the observed and calculated shuttle speeds together with the directly determined average loom speed during picking being given in Table XXVI.

Table XXVI

Timing of the Pick, Average Loom Speed during Picking, Observed and Calculated Shuttle Speeds; Loom 17

Band-taut position:			
Degrees top shaft before bottom centre:	+8°	−11°	−44°
Observed shuttle speed, feet per second	47·0	53·0	57·5
Calculated shuttle speed, feet per second	46·6	55·4	63·9
Average loom speed during picking, picks per min.	109	124	136

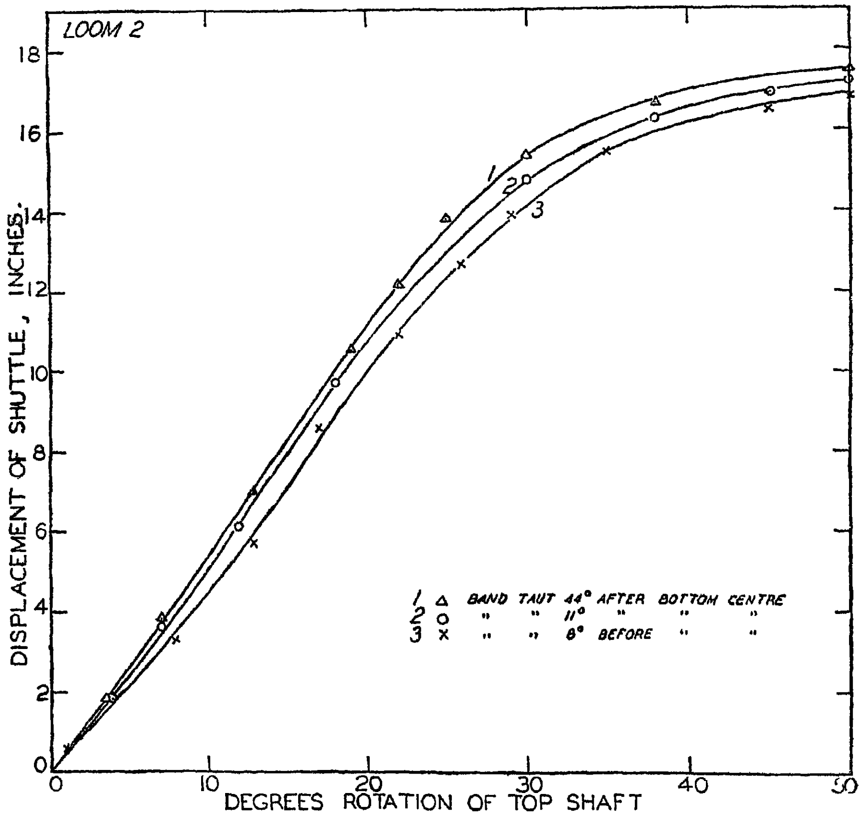


Fig. 15

Nominal displacement curves for various timings of the pick.

In this instance the actual loom speed during picking was used in the formula instead of the estimated value of 0.85 × the average loom speed, this being necessitated by the very large changes with timing of the average loom speed during picking for this loom.

As indicated in Tables XIII and XIV the mass of the shuttle does not appreciably affect the shuttle speed, this being also a necessary consequence of the theory.

Thus, as regards Lancashire looms, variations in shuttle speed can be qualitatively followed from the variations in the nominal movement and the absolute value of the speed can be calculated with fair accuracy by the application of the semi-empirical rule described.

Acknowledgments. Thanks are due to Mr. H. Airey and Mr. P. Sutton for assistance with the experimental work.

APPENDIX

MODIFICATION OF THE NOMINAL MOVEMENT OF THE PICKER BY THE MOVEMENT OF THE SLEY

Referring to Fig. 16, OX represents the picker spindle at the instant when the picking band is taut, and O is a fixed point on the picker. OY and OZ are perpendicular axes forming with OX axes of reference fixed relative to the loom frame. O′X′ represents the position of the picker spindle after completion of the effective part of the nominal movement of the picker, i.e. after about 30 degrees' rotation of the crank. O′ represents the new position of O and O′Q represents the nominal distance moved by the picker, Q being the point of intersection of O′X′ and OY, the picker spindle being assumed for simplicity to move in a horizontal plane. P, P′ are the positions of the effective end of the picking stick corresponding to positions O, O′ of the picker. Let the co-ordinates of P be (x, y, z), of P′ be $(x + X, y, z)$, and of O′ be $(a, b, 0)$.

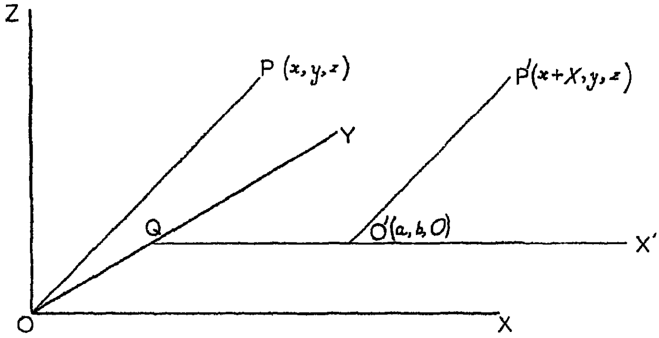


Fig. 16
Diagram representing the positions of the picking band, OP, and the picker spindle, OX, at the beginning and end of the shuttle acceleration period.

Then b is the backward movement of the sley which occurs during picking, and a is the nominal movement of the picker whose value we wish to obtain.

Neglecting the stretching of the picking band:

$$\text{OP} = \text{O}'\text{P}'$$

$$x^2 + y^2 + z^2 = (x + X - a)^2 + (y - b)^2 + z^2$$

$$\text{whence } a = X + x - (x^2 + 2by - b^2)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

It is seen from (1) that if $b = 0$, $a = X$, as would be expected, i.e. if the sley is stationary the nominal movement of the picker is the same as that of the end of the picking stick.

On a standard Lancashire loom, approximate values are $x = 7''$, $y = -1''$ to $-2''$, $b = 1\frac{1}{2}''$, so that $(2by - b^2) / x^2$ is sufficiently small for squares and higher powers to be neglected.

Hence we have approximately

$$a = X + \frac{b^2}{2x} - \frac{by}{x} \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

The effect of the timing can now be seen. Its chief effect is on y. Later timing of the band-taut position will cause the spindle to lie further back and diminish y algebraically; b will be little changed by the change in timing and so a larger value of $-by/x$ will result, and for a given change in y the change in a will be larger the smaller the value of x, that is, the shorter the picking band. Usually y is less algebraically than $b/2$ and hence $(b^2/2x - by/x)$ is positive and the nominal movement of the picker is usually greater than the nominal movement of the end of the picking stick.

REFERENCES

Catalogue of the Collections in the Science Museum, South Kensington, Textile Machinery; London, 1921, p 6.

[2] Galton, D " General Results of some Recent Experiments upon the Coefficient of Friction between Surfaces Moving at High Velocities." *British Association Report*, 1878, p. 438.

[3] Hanton, W. A " Mechanics of Textile Machinery," London, 1924, p. 162.

[4] Hanton, W. A *Textile Manufacturer*, 1930, **56**, 119

[5] Honegger, E. *Journ. Textile Inst*, 1933, **24**, T 421.

[6] Kilgour, R McK., Waring, R., and Boffey, H *Journ. Textile Inst.*, 1938, **29**, T 173

[7] Kilgour, R. McK, Waring R., and Boffey, H *Loc. cit.*, p. 187

[8] Oxley, A E *Shirley Inst Mem*, 1922, 1, 18, or *Journ Textile Inst*, 1922, 13, *Trans.* p 55

[9] Palmer, A *Textile Manufacturer*, 1937, **63**, 326

[10] Palmer, A, and Ramsdell F. *Textile World*, 1935, **85**, 881

[11] Vincent, J. J, and Howell, W T *Shirley Inst Mem*, 1939, **17**, 1; or *Journ Textile Inst.*, 1939, **30**, T103.

[12] Vincent, J J, and Howell, W. T *Loc cit*, p 17, or T 120

[13] Woodhouse, T., and Milne, T. " Jute and Linen Weaving," London, 1914, p 337

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2—THE CHECKING OF SHUTTLES IN POWER LOOMS

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ABSTRACT

The checking of shuttles has been studied by obtaining the displacement/time relation for the shuttle when being checked in the shuttle box. From this relation was obtained the maximum value of the retardation and the speed of impact of the shuttle with the picker. The position at which the shuttle came to rest was also observed. The maximum value of the retardation was found to vary from about 50*g*, for a 45-inch loom fitted with a controlled swell adjusted to stop the shuttle just short of the picker, to at least 220*g* for a 60-inch fast-reed loom with a plain swell (*g* is the acceleration due to gravity). The speed of impact of the shuttle with the picker was negligible with a controlled swell, but was high (up to 40 feet per second) when plain swells were employed The variation of the rest position of the shuttle over 1,000 picks was about ½ in. to ¾ in. The use of an accelerometer giving direct readings of the maximum retardation is described, and comparisons of results obtained by the two methods are made. It is shown that the accelerometer may fail to respond to high transient values of the retardation, but this does not impair its usefulness for comparative purposes.

INTRODUCTION

The nature of the motion of the shuttle while it is being checked is not ascertainable directly without recourse to special means of observation, and this doubtless accounts for the small amount of available information relating to checking and for its somewhat conflicting nature. Kilgour, Waring, and Boffey[4] have carried out some experiments on a fast-reed linen loom from which they conclude that " up to a loom speed of about 180 picks per minute the residual velocity of the shuttle on arrival at the picker at the back of the box must be considerable." This is in agreement with a deduction made by Hanton[1] in which he shows that a shuttle entering the box at about 43 feet per second would strike the picker with a speed of 41 f.p.s. Hanton considers the checking as occurring in two stages: one during which the swell alone acts, and the other during which the picker and check-strap act as well, the retardation in each stage being considered uniform. Wilmot,[7] on the other hand, assumes, without stating the grounds for his assumption, that the retardation takes place in a single stage, during which the motion is simple-harmonic. A third view is expressed in the International Correspondence Schools Reference Library,[2] where it is stated: " Before the shuttle touches the picker in the receiving box, the shuttle has already been checked to a great extent by the swell and the slightly narrowing width of the box." In no publication is there much discussion of what is the desirable form for the retardation to take and whether the motion described is satisfactory or not. The most explicit statement is that of Woodhouse and Milne,[8] who, in reference to the check-strap, state · " a travel of 3 inches in a 45-inch reed space loom is not too much. If the travel be short and the shuttle be checked suddenly, it is practically equivalent to having no check-strap at all, and results in the shuttle rebounding, in broken cops, and in ravelled pirns Checking should not begin, however, until the shuttle has actuated the warp protector."

It is not difficult to lay down the conditions which the checking should fulfil They are: (1) the shuttle should come to rest in contact with the picker at the same place in the shuttle-box after each pick, (2) the maximum value of the retardation should be kept as small as possible, and (3) the speed of impact of the shuttle with the picker should be as small as possible. These conditions are not entirely independent since (3) is largely implied by (2), for impact always results in rapid retardation. The first condition aims at ensuring that the shuttle speed on the following pick has a constant value, and that weft feelers, where fitted, produce a minimum of waste; the second aims at reducing to a minimum the force tending to displace and disintegrate the weft package; and the third condition aims at reducing the rate of wear of the picker. The second condition is the most important because too rapid retardation may lead to undesirable restriction of the loom speed or the size of the weft package, or may require the fitting of new shuttle tongues to suit new deliveries of cop weft differing slightly in bore so as to ensure that the cop is held firmly enough to withstand the tendency to displacement during checking

For a given shuttle speed, the maximum retardation during checking cannot fall below the value corresponding to uniform retardation over the whole length of the shuttle-box, and this is the form of retardation at which to aim. Such retardation has the effect of prolonging the time for the shuttle to leave the shed, and hence for the same timing of the looma higher initial shuttle speed is necessary. This effect has been exaggerated in technical writings to such an extent that it is usually recommended that checking should not begin until the shuttle has completely left the shed, but, as the calculation given in Appendix I shows, if the whole shuttle-box is employed for retarding the shuttle uniformly, the extra time taken for the shuttle to leave the shed completely, compared with that taken with the recommended arrangement, is only about 7 per cent. of the total traverse time, and if uniform retardation begins when six inches of the shuttle remain in the shed then the traverse time is increased by less than 2 per cent. Where the shuttle speed is already high, increasing it by 7 per cent. might be undesirable, but usually this would not be serious. Certainly an increase of 3 per cent., or 1 2. f.p s. on 40 f p.s, corresponding to checking beginning while 8 inches of the shuttle remained in the shed, would always be tolerable, and yet the improvement in the checking would be very large; for, as will appear later about 6 inches of the shuttle-box are used for checking at present, whereas with checking beginning when 8 inches of the shuttle remained in the shed there would be available about 14 inches for the checking of the shuttle, which if correctly used would reduce the maximum checking force to about one-eighth of the value occurring at present with plain swells.

It was with the object of confirming or refuting the views expressed by the authors cited above, and of testing how nearly checking in practice approaches the ideal conditions laid down, that the present work was undertaken. It is hoped, too, that the methods of investigation employed may prove useful for testing the value of new types of checking mechanism. Such tests would establish, quickly and accurately, results which otherwise could only be obtained with difficulty by prolonged and careful collection of information relating to the durability of pickers, amount of weft waste, and the frequency of shuttle traps

METHOD AND APPARATUS

The position of the shuttle when at rest in the shuttle-box was determined by means of a spring-seated needle in the way already described in the paper " An Experimental Study of Shuttle Projection "[5]

The speed of the shuttle before and during checking was measured exactly as described in that paper, except that instead of the circular hole in the back of the shuttle-box through which shone the beam of light marking the position of the shuttle, a vertical slot, $\frac{1}{16}$ inch wide and 1 inch long, was employed, which allowed observations to be made with the sley moving normally.

The maximum value reached by the retardation was measured directly in some instances by means of the accelerometer shown in Fig. 1. Fitted to the shuttle after the removal of the tongue, the accelerometer is held by means of special grips G_1 and G_2 adapted to fit shuttles of different widths. Each grip consists of a steel block fitted with three small fixed steel spikes on one side, and a large spike on the other which screws in or out of the block The large spike is screwed out until it enters one wall of the shuttle while the three small spikes enter the other, and movement of the block is completely prevented As an alternative to the grip near the end of the shuttle at which the heel of the shuttle-tongue would normally be, it is convenient to use a block shaped like the heel of a shuttle-tongue and to anchor it with a hinge-pin Connecting the two grips G_1 and G_2 is a stainless steel rod R, partly of square and partly of circular cross-section, upon which a steel compression spring S fits loosely with one end resting against a knurled nut N, and the other end against a brass block M The nut N mates with a threaded portion of the rod R and is locked by a locking ring L The brass block M is an easy sliding fit on R, which in this region is of square cross-section, and is held by the compression spring against the grip G_2. Mounted on a pivot fixed in G_2 is a light pointer P, balanced about its axis of rotation, and prevented from rotating by a small adjustable frictional resistance applied by a spring on the under side of the grip G_2. When the block M is in contact with the grip G_2 the pointer P is set to rest against an extension A fixed to M, and if M moves away from G_2 the pointer is rotated and remains displaced when M resumes its original position The pointer thus serves as a sensitive indicator of whether M has been momentarily displaced, since the end of the pointer magnifies the movement of M by four. The displacement of the pointer may be read off on a scale attached to G_2.

When the shuttle is accelerated in the direction G_1 to G_2, the block M will separate from G_2 unless the force applied by the compression spring is equal to, or greater than, the mass of M multiplied by the acceleration of the shuttle. Any such movement is indicated by the pointer P, and the method of use is to compress the spring just enough to prevent separation of the mass and the stop For very accurate work the point of balance may be obtained by noting the deflection of the pointer for a number of lengths of the spring when insufficiently compressed to achieve a balance and then obtaining by extrapolation the length of the spring corresponding to zero deflection of the block M. When this method is used, and there is some variation in the retardation from pick to pick, the extrapolated value will approximate to the average value of the retardation The compression of the spring is measured on the scale T which for a given spring and block may be calibrated in units of g, the acceleration due to gravity. (The scale shown in the photograph had still to be calibrated.)

Since the mass of the spring is not negligible, the force applied by the spring to the block M for a given amount of compression is less dynamically than it is statically. The calculation in Appendix II shows that the correct value of the acceleration is obtained by adding half the mass of the spring to the mass of the block, and using the static force corresponding to the observed compression.

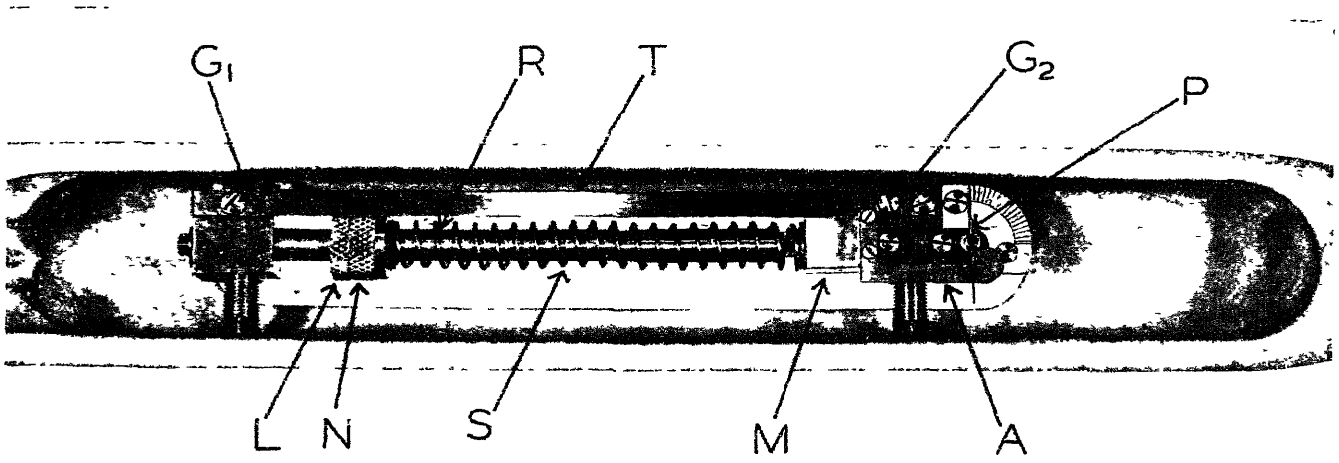


Fig. 1.
Photograph of accelerometer in position in a shuttle.

The total mass of the accelerometer is roughly the same as that of a shuttle tongue, pivot and spring, together with a full cop. This ensures that the shuttle under test has about the same mass as the normal shuttle containing a full cop, the retardation of the shuttle in this condition being of most interest. In using the accelerometer this point has to be checked, particularly where large cops are used, because if the mass of the shuttle containing the accelerometer were different from normal, its retardation would be different. If necessary the shuttle is weighted for the purpose of the test.

RESULTS

Loose-reed Loom with Normal Swell and Check Strap

Experiments were carried out on a Wm. Dickinson 45-inch reed-space, loose-reed loom, running empty at 200 picks per minute. The results for such a loom may be taken as typical of its class

Variation of the shuttle's rest position. With a cop of weight 1 oz. in a shuttle of weight 7.4 oz. the range of variation in the shuttle's rest position occurring while the loom ran for 1,000 picks (i.e there were 500 entries of the shuttle into the particular box under observation) was 0.55 inch, and when the shuttle was empty was 0.49 inch. The two ranges overlapped—the empty shuttle, on the average, not going so far into the box as the full one—and covered between them a distance of 0.71 inch

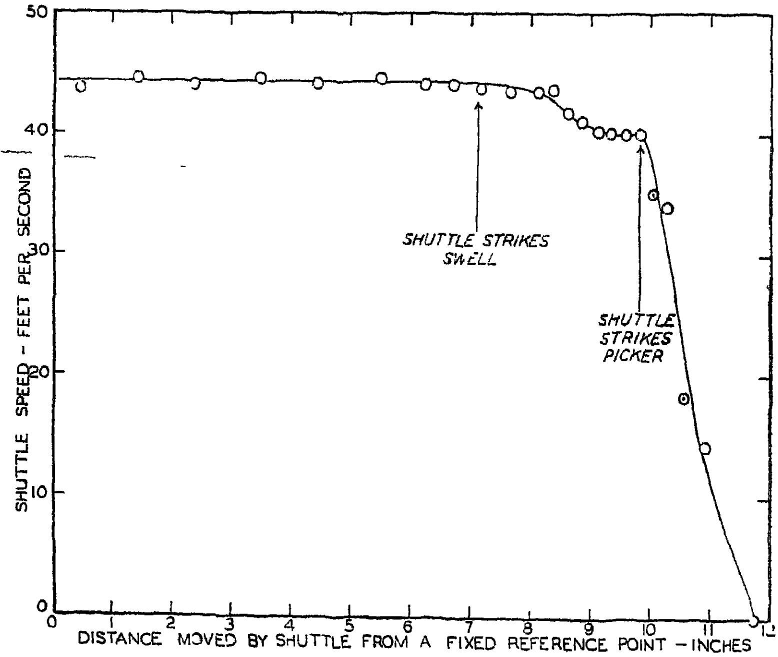


Fig. 2

Relation between speed of shuttle and distance moved during checking on a loose-reed loom with plain swells.

Speed changes. The changes in speed which occurred during checking when an empty shuttle of weight 7.4 oz. was used are shown in Figs. 2 and 3 where the speed is plotted against distance and time, respectively. The loom was set exactly as it had been when running with warp and weft. The position at which the shuttle comes to rest can be determined accurately, but not the time, owing to the slow movement of the shuttle just before motion ceases For this reason Fig. 2 is more complete than Fig. 3.

It will be seen from Fig. 2 that the speed of the shuttle remained unchanged until it was within 4.65 inches of its rest position. During the next 2.75 inches of travel, the retardation, which resulted from the action of the swell alone, was slight and led to a fall in speed of only 10 per cent. Such a retardation is equivalent to a uniform retardation of 25*g* (where *g* is the acceleration due to gravity) over the same distance and this would be produced by a constant resistance of 11.6 lb. weight. The checking became really effective from the time when the shuttle struck the picker, when the inertia of the picker and check-strap, the friction of the check-strap on the picker-spindle, and the friction of the swell, were all acting together. The effect of this resistance was to bring the shuttle to rest from a speed of 40.0 feet per second in 1.90 inches. This restardation was equal to a uniform retardation of 157*g* over the same distance and this retardation would be produced by a resistance of 73 lb. weight.

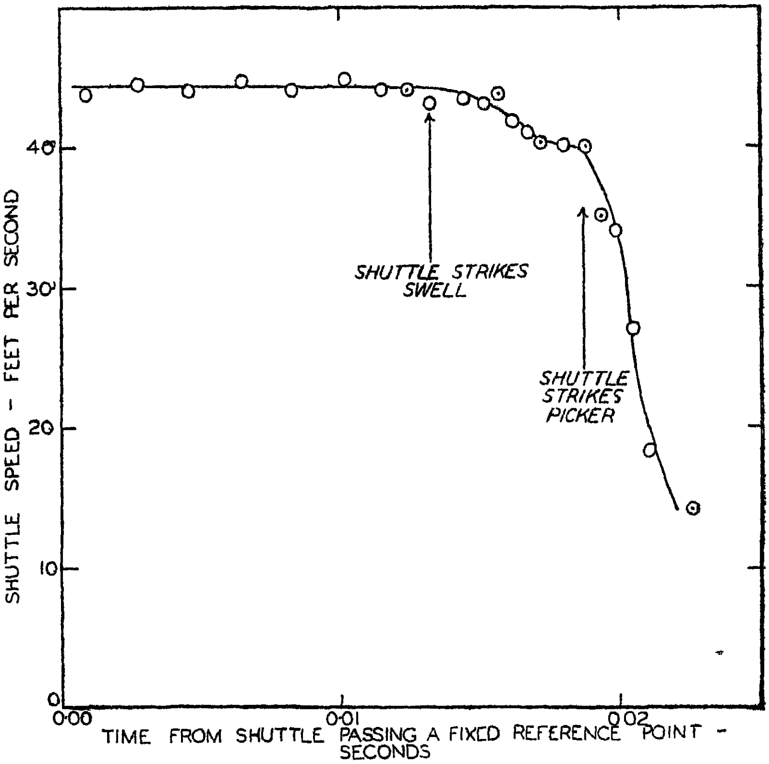


Fig. 3
Relation between speed of shuttle and time during checking on a loose-reed loom with plain swells

The non-uniformity of the retardation is apparent from the deviation from a straight line of the curve in Fig. 3. From the same figure it appears that the total time during which checking took place was about 0.01 second, corresponding to about 12° rotation of the top shaft, the average loom speed during checking being 196 picks per minute.

Speed of impact of the shuttle with the picker The shuttle struck the picker with a speed of 40.0 feet per second, which was 90 per cent. of the unchecked speed.

Loose-reed Loom with a Controlled Swell

The conditions were the same as in the previous section except that the ordinary swell and check-strap were replaced by a controlled swell, and the loom was run for single picks only. It should be noted that some of the settings would have been too critical to have allowed of satisfactory continuous running under industrial conditions in view of inevitable variations in the speed of the in-coming shuttle when a warp is present The controlled swell was of the type where an arm operated by the crank-arm increased the swell pressure during the time when the shuttle was entering the box, but reduced it to a very small value at other times, in particular when the shuttle was leaving the box. In this way it was possible to apply a considerable retarding force to the shuttle during checking without adding to the force required to pick the shuttle out of the box.

Variation of the shuttle's rest position For this experiment the swell was set by an experienced overlooker to what he considered the correct setting, his criterion being that the empty shuttle should just reach the picker, which condition he judged by placing his thumb behind the picker while the loom was running. This setting would not necessarily be correct if a warp were present.

With a cop of weight 1 oz. in a shuttle weighing 7.4 oz the range of variation in the shuttle's rest position occurring while the loom ran for 1000 picks was 0 38 inch and when the shuttle was empty was 0.40 inch The two ranges covered between them a distance of 0.58 inch.

Speed changes. The changes in speed occurring during checking are shown in Figs. 4 and 5, where the speed is plotted against distance and time, respectively. In Fig. 4 the results for three different settings of the swell are plotted, and in Fig. 5 the corresponding results for the two extreme settings. The slight differences in the unchecked speeds are due to experimental errors and to slight changes in the loom from one occasion to another, and are of no significance. Fig. 4 shows that with setting 1 the shuttle just reached the picker at the outer end of the box after being retarded over a distance of 6.0 inches. This retardation was equivalent to a uniform retardation of 45*g* which would be produced by a constant resistance of 21 lb. weight. With settings 2 and 3 greater pressure was applied by the swell, and the rest position of the shuttle fell short of the picker by 0.7 inch and 1.3 inch, respectively, the retardations being equivalent to uniform retardations of 49*g* and 61*g*, which would result from resistances of 23 lb. weight and 28 lb. weight, respectively. It will be observed that the minimum value of the retardation is obtained when the shuttle just reaches the picker, that is, when all the retardation is effected by the swell. If the swell-pressure is increased above the value necessary to achieve this, then the retardation takes place over a shorter distance and reaches a higher value. On the other hand, if the swell-pressure is reduced, impact with the picker occurs and this also leads to a higher value of the retardation.

The graphs in Fig. 5 show that the retardation was more uniform than with the standard swell and check-strap (cf. Fig. 3). The times taken to check the shuttle for settings 1 and 3 exceeded 0 013 second, equivalent to 15° rotation of the top shaft.

Speed of impact of the shuttle with the picker. For setting 1 the speed of impact was practically zero, and for the other two settings impact did not take place.

Fast-reed Loom with Normal Swell and Check Strap

Experiments were carried out on a Pilling 60-inch reed-space fast-reed loom running at 181 picks per minute.

Variation of the shuttle's rest position. With a cop of weight 1 oz. in a shuttle weighing 10.3 oz. the range of variation in the shuttle's rest position occurring while the loom ran for 1,000 picks was 0.20 inch, and when the shuttle was empty was 0.22 inch. The two ranges covered a total distance of 0.30 inch.

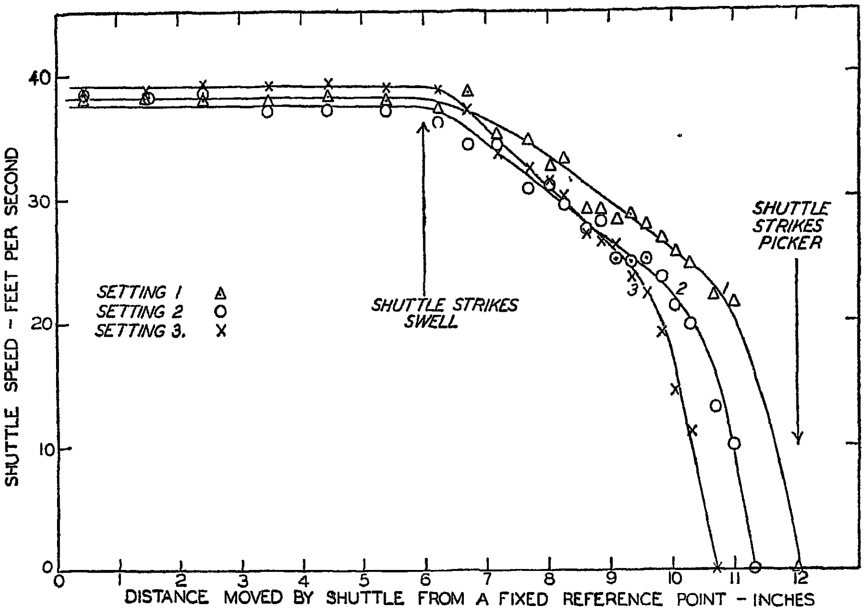


Fig 4
Relation between speed of shuttle and distance moved during checking on a loose-reed loom with controlled swells

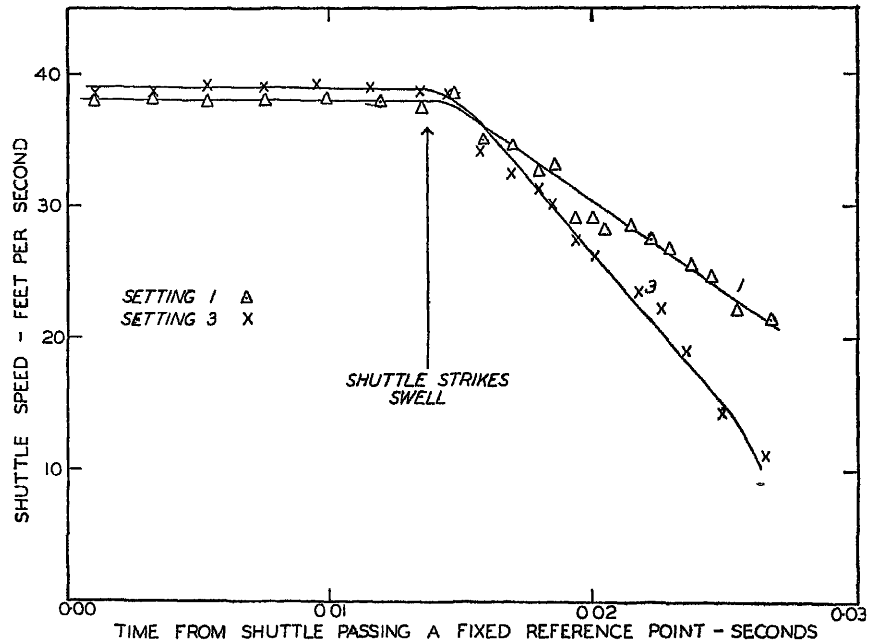


Fig. 5
Relation between speed of shuttle and time during checking on a loose-reed loom with controlled swells.

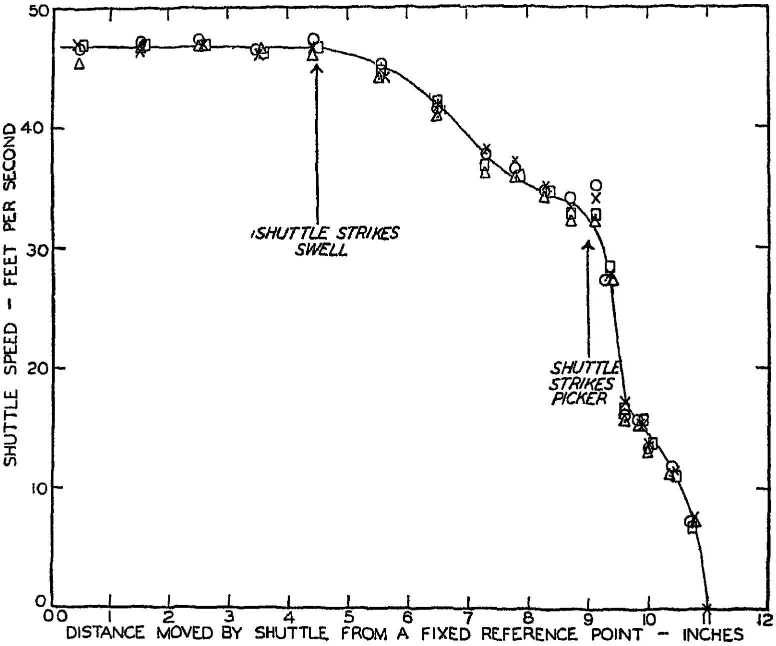


Fig. 6.

Relation between speed of shuttle and distance moved during checking on a fast-reed loom

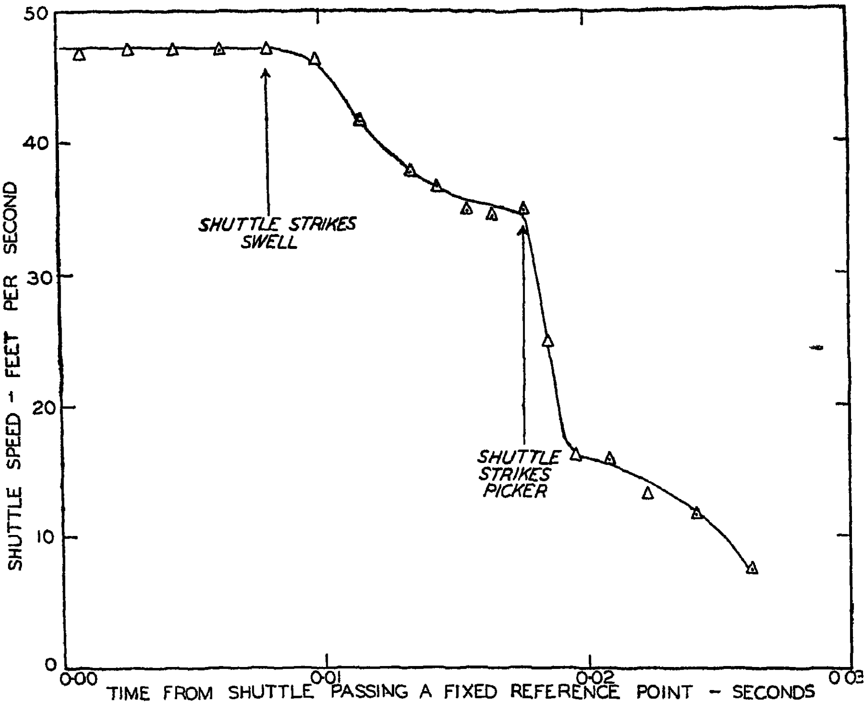


Fig. 7.

Relation between speed of shuttle and time during checking on a fast-reed loom

Speed changes. The changes in speed which occurred during the checking of an empty shuttle of weight 7.6 oz. are shown in Figs. 6 and 7. In Fig. 6 four repeated sets of observations are plotted against distance, and in Fig. 7 one set is plotted against time. The retardation took place over a distance of 6.5 inches, in about 0.02 second, and occurred in three stages. In the first stage, during which the swell alone was acting, the shuttle moved 4.5 inches and the shuttle speed was reduced by 32 per cent. This retardation was equivalent to a uniform retardation of 47*g* acting over the same distance, which would be produced by a force of 22.3 lb. weight.

The second stage included impact with the picker and during this stage the shuttle moved 0.65 inch and lost a further 33 per cent of its unchecked speed. This retardation corresponded to a uniform retardation of 219*g*, which would be produced by a force of 104 lb. weight. In the last stage, extending over 1.35 inches, the friction of the check-strap and the swell were both acting. The retardation produced was equivalent to a uniform retardation of 39*g* which would be produced by a force of 18.5 lb. weight. The irregularity of the retardation is shown by the non-linearity of the curve in Fig. 7.

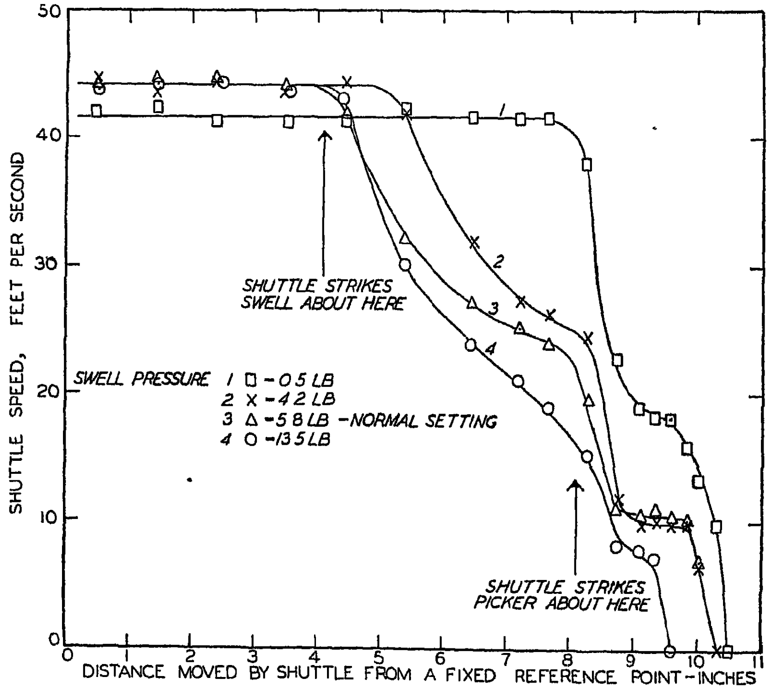


Fig. 8.

Relation between speed of shuttle and distance moved during checking on a fast-reed loom for various swell pressures.

Speed of impact of the shuttle with the picker. The shuttle struck the picker with a speed of 32 feet per second or 68 per cent. of the unchecked speed. The effect of increasing the tension in the stop-rod springs was to reduce the speed of impact of the shuttle with the picker and so reduce the retardation occurring at that stage. This result is shown in Fig. 8 where it will be seen that when the swell-pressure was increased from 0.5 lb. weight to 13.5 lb. weight the impact speed was reduced from 96 per cent. of the unchecked speed to 34 per cent., and the fall in speed in the half-inch following impact dropped from 16 f.p.s. to 5 f.p.s. It will be noticed that at the lowest swell-pressure the unchecked shuttle speed was less than with the higher swell-pressures. This was due to rebounding of the shuttle in consequence of the inadequate checking and this caused the picking to be slightly defective.

Results Obtained with the Accelerometer

Using the loose-reed loom and the controlled swell already referred to, set to various pressures, some comparisons were made of the maximum retardation recorded by the accelerometer with the maximum value obtained indirectly from the photographic measurements. The acceleration of the shuttle was calculated from the slope of the speed/distance curve in the form vdv/ds where v is the speed and s the distance traversed. Since v involves a differentiation of s with respect to time, the value of the acceleration involves two differentiations and its accuracy cannot be high. Another factor that may lead to a difference between the two values, arises from the retardation measured photographically being the value for a single pick, whereas the retardation obtained by the accelerometer is approximately an average value for a number of picks, since the point of balance was obtained by extrapolation. The two sets of values are compared in Table I. It will be seen that for tests 1 and 2 the results obtained by the two methods are in quite close agreement, but for the remaining tests the accelerometer readings are all less than the corresponding values obtained indirectly, although the two methods place the retardations in the same order. Examination of the speed/distance curves revealed that in the first two tests the rate of change of the retardation with distance in the neighbourhood of the maximum was much less than in the remaining tests. It seems probable, therefore, that the accelerometer fails to respond to high transient values of retardation.

Table I

Maximum Retardation obtained Photographically and by Accelerometer

Test No	1	2	3	4	5
Retardation, by accelerometer .	89*g*	112*g*	103*g*	94*g*	79*g*
Retardation, from v, s curve .	94*g*	108*g*	145*g*	126*g*	110*g*

For mill investigations the accelerometer possesses obvious advantages over the other method. Some typical results are given in Table II. An early model of the accelerometer, calibrated in arbitrary units, was used in one investigation, but for comparative purposes this was no disadvantage. The looms designated "unsatisfactory" had given cause for complaint in respect of checking on account of the tendency to break cops in one case, and because of the noise in the other, and comparisons were made with similar looms that were considered satisfactory. It will be seen that the maximum retardation was appreciably greater in the unsatisfactory looms than in the corresponding satisfactory looms.

Table II

Measurements of the Maximum Retardation on Looms at Mills

	Loom No	Retardation	Condition
Mill A	171	75 arbitrary units	Satisfactory
	137	96	Satisfactory
	152	107	Satisfactory
	144	134	Unsatisfactory
	126	144	Unsatisfactory
Mill B	24	125*g*	Satisfactory
	23	157*g*	Unsatisfactory

The accelerometer was also used to test the effect of gouging a hole in a new picker. It is commonly asserted that if a hole is not gouged, cops will be broken or knocked off the shuttle tongue by the impact of the shuttle with the picker,[3] which is equivalent to saying that the gouging of a hole reduces the maximum retardation. Experiments were carried out with the loose-reed loom described above fitted with a normal check-strap and swell. Each side of a picker was used in turn ; one was gouged, the other not. Each side was used five times alternately with the other for a sufficient number of single picks to determine the retardation with the accelerometer. In the course of the test a hole was formed in the ungouged side, but its diameter and depth were 5 mm. and 2 5 mm., respectively, which were both considerably smaller than the corresponding dimensions, 13 mm. and 9 5 mm., of the hole in the gouged picker. The average value of the retardation was the same whichever side of the picker was used, suggesting that gouging had no appreciable effect.

DISCUSSION OF RESULTS

Although there is considerable variation from loom to loom in the industry in respect of the construction and setting of the shuttle-boxes, the physical dimensions of the parts are sufficiently alike for broad conclusions to be based on the results of the experiments performed on the two particular looms described.

The first point that emerges is that a variation in the shuttle's rest position of from half to three-quarters of an inch must be quite common, and that of this variation less than one-quarter of an inch can be attributed to the difference in mass between a full and empty shuttle. Such variation will affect the picking to a varying extent depending on the nature and the extent of the nominal picking movement, and although obviously not serious for most of the time, it must add to the difficulty of ensuring on every pick a satisfactory traverse of the shuttle combined with a minimum shuttle speed. The effect on the operation of weft feelers may be more serious, to an extent depending on the particular design, and may lead either to excessive waste, or to failure of the loom to stop before the weft is exhausted The fast-reed loom tested was better in this respect than the loose-reed loom, but it would be unwise to generalise from this

The maximum values of the retardation cannot be known with certainty, since the measurements are not sufficiently accurate, but it is safe to say that the maximum retardation was at least 157*g*, 45*g*, and 219*g* respectively, for the loose-reed loom with plain swells, the loose-reed loom with controlled swells, and the fast-reed loom with plain swells, these values having been calculated on the assumption of uniform retardation over the relevant stage of checking With the controlled swell the checking was fairly uniform so that the maximum retardation did not probably exceed 45*g* by a great deal, but in the other two cases the maximum retardations may have been considerably greater than the figures given The most striking fact is the superiority of the controlled swell in keeping down the maximum retardation of the shuttle The reason for this is the absence of impact at high speed with the picker. The higher value of the retardation with the fast-reed loom probably results from the greater mass of the picker and check-strap in relation to the mass of the shuttle, this arising from the greater width of loom.

On both looms, when fitted with plain swells, the speed of impact of the shuttle and picker was high The fast-reed loom was superior in that a larger fraction of the unchecked speed was destroyed before impact, and this result is probably generally true since the swells on fast-reed looms are longer than on loose-reed looms due to the absence of the box flap, and, moreover, the swells combined with the stop-rod mechanism provide a more effective check than the simple swell on the loose-reed loom. The controlled swell was much superior to both the others since the speed of impact with the picker was negligible.

It is clear from these results that the checking on looms fitted with plain swells is very far from satisfying the conditions laid down in the Introduction. The controlled swell is satisfactory in respect of the speed of impact with the picker and is better than the plain swell in respect of the maximum retardation, but since the retardation takes place over only 6 inches compared with a possible 14 inches, it is clear that the lowest possible retardation has not been achieved. Assuming an unchecked speed of 40 f.p.s., uniform retardation to rest over a distance of 14 inches would have the value of 21*g* This compares with a value of about 45*g* occurring with the controlled swell, and values greater than 157*g* and 219*g* occurring with the two plain swells. The apparent superiority of the controlled swell prompts the query as to why it is not more widely used. The answer would appear to be that if the swell is set so that during normal running the shuttle just reaches the picker, then if the shuttle speed is low for any reason (the most common being slow starting of the loom) the shuttle will stop short of the picker and on the next pick the shuttle speed will be low, leading possibly to a shuttle trap. With the plain swell in similar circumstances the shuttle will reach the picker and the next pick will be little affected. There are various ways in which the difficulty with the controlled swell can be met, but it is not proposed to discuss them here.

The results show that the statements of Kilgour, Waring and Boffey,[4] and of Hanton[1] (cited in the Introduction), to the effect that with the plain swell there is little retardation of the shuttle before it reaches the picker, are substantially correct, but there seems to be no justification for Wilmot's assertion[7] that the motion of the shuttle during checking is simple harmonic; while the statement in the International Correspondence Schools Reference Library,[2] that the shuttle has been checked to a great extent before reaching the picker, is definitely wrong in relation to the plain swells to which it referred.

In view of the inadequacy of existing swells it would not be profitable to determine more accurately, or for a larger number of looms, the exact form of the retardation. Further work in this field can best be devoted to improving swells and testing their behaviour, for which work the shuttle-position indicator, the accelerometer, and direct-reading speedometer,[6] will suffice as instruments of observation.

Acknowledgments. Thanks are due to Mr H. Airey and Mr. P. Sutton for assistance with the experimental work; and to Mr. H. B. Cummings for preparing drawings of the accelerometer, and to Mr. H. B. Williams and the Shirley Institute Workshop staff for making the accelerometer and other apparatus.

APPENDIX I.

THE EFFECT ON THE TIME OF TRAVERSE OF THE SHUTTLE OF CHECKING THE SHUTTLE WHEN PARTIALLY IN THE SHED, ASSUMING UNIFORM RETARDATION

Let v = the shuttle speed when the leading tip of the shuttle enters the shuttle-box,
l = the length of the shuttle,
b = the length of the shuttle-box,
c = the distance the shuttle penetrates the box before checking begins.

Then while traversing the distance c the shuttle retains its initial speed and hence the time taken is c/v It is assumed that thereafter the shuttle is uniformly retarded in such a way as to come to rest at the outer end of the box. The magnitude of this retardation is therefore $\frac{v^2}{2(b-c)}$. With this retardation, the time taken for the remainder of the shuttle to leave the shed is t where $l-c = vt - \dfrac{v^2t^2}{4(b-c)}$

$$\text{whence } t = \frac{2(b-c) - 2\sqrt{(b-c)(b-l)}}{v} \qquad \ldots\ldots \tag{1}$$

the negative square root being taken since the time taken to traverse the distance $l-c$ cannot exceed the time taken to traverse the distance $b-c$, which is $\dfrac{2(b-c)}{v}$.

The total time, T, for the whole shuttle to enter the shuttle-box is

$$\text{therefore } T = \frac{c}{v} + \frac{2(b-c) - 2\sqrt{(b-c)(b-l)}}{v}$$

$$\text{i.e. } T = \frac{2b - c - 2\sqrt{(b-c)(b-l)}}{v} \qquad \ldots\ldots \tag{2}$$

When no checking occurs until the whole shuttle is in the box then $c=l$, the time for leaving the shed is a minimum, and $T_{\min} = l/v$ .. .. (3)

When checking starts immediately the shuttle reaches the mouth of the box, then $c=0$, the time for leaving the shed is a maximum and

$$T_{\max} = \frac{2b - 2\sqrt{b(b-l)}}{v} \qquad \ldots\ldots \tag{4}$$

Substituting typical values for a 45-inch loom: $v=40$ f.p.s., $l=14$ in.; $b=20$ in.

then $T_{\min} = 0{\cdot}0292$ sec.
and $T_{\max} = 0{\cdot}0376$ sec.
$T_{\max} - T_{\min} = 0{\cdot}0084$ sec

The minimum traverse time for the 59 inches comprising 45 inches of reed-space and 14 inches of shuttle $= 0{\cdot}123$ sec.

Therefore $T_{\max} - T_{\min} = 7$ per cent of total traverse time

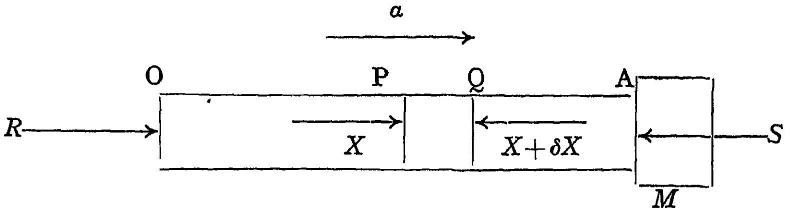
When $c=8$ inches, $T=0{\cdot}0314$ sec., and the total traverse time is 2 per cent. greater than the minimum

When $c=6$ inches, $T=0{\cdot}0326$ sec, and the total traverse time is 3 per cent. greater than the minimum.

APPENDIX II.

ACCELEROMETER: CORRECTION FOR THE MASS OF THE SPRING

Consider the spring as consisting of a uniform elastic rod OA with the mass M attached at A and the end O fixed in the shuttle.



Let l = the unstrained length of the rod,
m = the mass per unit length of the rod in the unstrained state,
λ = the thrust in the rod ÷ the compression per unit length,
a = the acceleration of the rod in the direction O to A.

When the shuttle has the acceleration a,

let R = the force applied to the rod at O
S = the force applied to the rod at A
OP $= x$
OQ $= x+\delta x$
X = the thrust applied to the element PQ at P
$X+\delta X$ = the thrust applied to the element PQ at Q.

Then the unstrained length of the element PQ is $\frac{\lambda\delta x}{\lambda - X}$, and its mass is $\frac{m\lambda\delta x}{\lambda - X}$.

Therefore, for the motion of PQ, $-\delta X = \frac{m\lambda\delta x a}{\lambda - X}$

Whence, since $X=R$ when $x=0$,

$$2m\lambda a x = (X+R-2\lambda)(X-R) \qquad \text{(1)}$$

Whence, when $X=S$,

$$x = \text{length of strained rod} = \frac{(S+R-2\lambda)\,(S-R)}{2m\lambda a} \qquad \text{(2)}$$

For the motion of the whole rod $R-S=mla$ .... (3)

For the motion of the mass M, $S=Ma$ .... (4)

Substituting for R and S from (3) and (4) in (2),

$$\text{length of strained rod} = \frac{[Ma+(M+ml)\,a-2\lambda]\,(-mla)}{2m\lambda a}$$

$$= \frac{l}{2\lambda}[2\lambda - a(2M+ml)] \qquad \text{(5)}$$

Therefore, the compression of the rod per unit length is

$$1 - \frac{2\lambda - a(2M+ml)}{2\lambda}$$

$$= \frac{a(2M+ml)}{2\lambda}$$

The static thrust corresponding to this compression per unit length is $a(M+ml/2)$, i.e., the compression is equivalent to that produced in a massless rod by the acceleration a of a mass equal to M plus half the mass of the rod.

REFERENCES

[1] Hanton, W A *Mechanics of Textile Machinery*, London, 1924, p 172.
[2] *International Correspondence Schools Reference Library*, London, Vol. 131, Section, 35, p. 34
[3] *Ibid* Section 38, 21
[4] Kilgour, R McK., Waring, R, and Boffey, H. *Journal of the Textile Institute*, 1938, 29 T180,
[5] Thomas, I. H., and Vincent, J J. Preceding *Memoir*, p. 282.
[6] Thomas, I H., and Vincent, J J. Following *Memoir*, p 321.
[7] Wilmot, R H. *Theory and Electrical Drive of the Loom*, London, 1931, p. 49.
[8] Woodhouse, T, and Milne, T. *Jute and Linen Weaving*, London, 1914, p. 517.

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3—AN INSTRUMENT FOR THE DIRECT MEASUREMENT OF SHUTTLE SPEED

By I H. THOMAS and J. J VINCENT

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ABSTRACT

An instrument is described which can be fitted into any shuttle to measure its speed. The principle of the instrument, of which the theory is given, is based on the fact that a helical spring, moving longitudinally, with a mass attached to the leading end, will extend if the other end is suddenly stopped The stopping is effected by impact of the shuttle with a fixed block of lead. The extension of the spring is directly proportional to the shuttle speed and is not appreciably affected by the shape of the shuttle tip or the mass of the shuttle

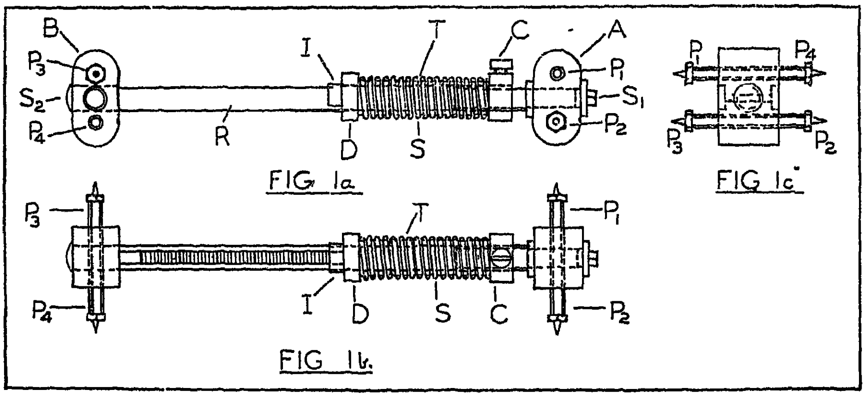
INTRODUCTION

Methods of measuring the speed of the shuttle in a power-loom have been described by several workers, [1, 2, 4] The apparatus used with each method was intended primarily for research purposes and was not adapted for obtaining rapid results in a weaving shed. For observations on a large number of looms, and for general industrial use, a quicker and simpler method is required One such method—the only method published to date —is the use of the semi-empirical formula given by Thomas and Vincent,[5] which involves merely a determination of the loom speed and the *nominal* movement of the picker, i e., the movement of the picker for a given rotation of the top shaft by hand The drawbacks to the use of this formula are that errors up to ± 10 per cent may occasionally arise, and the formula may not apply to looms of unusual type or to looms with abnormal nominal movements of the picker Moreover, it is the initial speed only of the shuttle that can be estimated in this way What is needed, therefore, is a robust instrument, easily applied to any loom, which will give a direct reading of the shuttle speed with reasonable accuracy. The instrument now to be described has been designed to meet these requirements.

THE INSTRUMENT AND ITS USE

Description

The construction of the instrument is shown in Figures 1(a) (front elevation), 1(b) (plan), and 1(c) (end view). Two red fibre or light alloy blocks A and B are rigidly connected by a stainless steel rod R which is held by screws S_1 and S_2 at each end. A helical steel extension spring S, initially free from stress, and not close-coiled, lies along the rod between the blocks. The spring consists of 23 coils of No. 18 S W.G. wire of internal diameter $\frac{11}{32}$-inch, of which 17 coils, of total mass 3·99 grams, are operative. One end of the spring is attached, by screwing and soldering, to a small cylindrical collar C which is threaded internally and mates with a threaded portion of the rod R The other end of the spring is attached in a similar manner to another steel collar D which is free to slide along the rod. The mass of D together with the idle coils attached to it and the solder fixing them is 4·71 grams. Any extension of the spring is indicated by the movement of a split cylindrical sleeve I, made of thin spring steel, which is pushed along the rod R by the collar D. The indicator I grips the rod R and in virtue of the friction set up remains at the point to which it is pushed. It thus indicates the maximum displacement of the collar D. The indicator requires to be re-set before each observation by placing it in contact with the collar D. The movement of the indicator is measured on a scale engraved on a flat on the rod. The position of the collar C is made adjustable so as to be able to bring the initial reading back to zero if the unstrained length of the spring changes, and a set-screw is provided to lock it in the desired position. Contraction of the spring, which otherwise would occur when the shuttle is accelerated during picking, is prevented by a tube T which is fixed to the collar C and lies inside the spring.



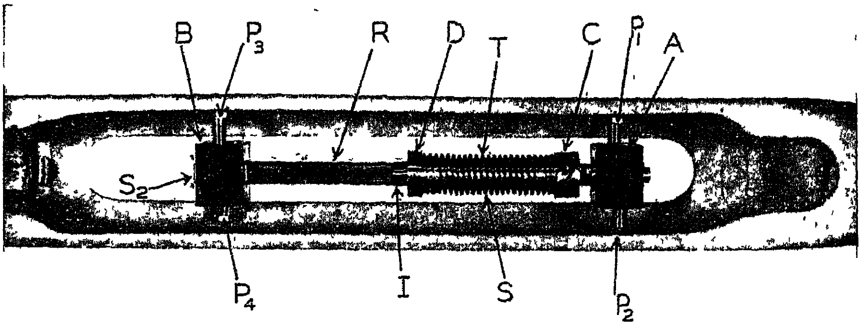


Fig 1(d)

Fig 1
Shuttle Speedometer

The instrument is fitted into the shuttle the speed of which is required, after removal of the shuttle tongue, by means of the pointed steel pins P_1, P_2, P_3 and P_4, which screw into the blocks A and B, and when partially screwed out penetrate the front and back walls of the shuttle As an alternative to the block and pins near the end of the shuttle at which the heel of the shuttle-tongue would normally be, it is convenient to use a block shaped like the heel of a shuttle-tongue and to anchor it with a hinge-pin. The whole instrument is made as light as possible by using red fibre, or light alloy, for the blocks A and B and hollowing out the rod R where it is not threaded in order to minimise the force on these pins when the shuttle is brought suddenly to rest.

The instrument is placed in the shuttle with the collar D nearer the leading tip than the collar C. The speed is measured by bringing the shuttle suddenly to rest by impact with a fixed lead block. This extends the spring momentarily and the indicator records the maximum extension attained As will appear later this extension, e, is directly proportional to the speed of the shuttle, v , by suitable calibration the speed may be read off directly.

Method of Use

It is usually most convenient, particularly if a warp is present, to measure the speed of the shuttle as it enters the shuttle-box The speed at this point is not necessarily the same as the speed with which the shuttle leaves the opposite box, but in an empty loom, or one where the passage of the shuttle is unobstructed, up to about 60 inches in reed-space, there is little difference between the two speeds If desired, the method can be adapted to measure the speed of the shuttle at any point between the two shuttle-boxes, apart from such restrictions as the presence of a warp may impose, but for many comparative purposes this is not necessary.

The shuttle containing the speedometer is brought to rest by impact with a cube of lead of side 1 inch clamped about half-way along the shuttle-box. The position of the lead block should be such that the shuttle has not made contact with the swell before impact takes place, if it is the unchecked shuttle speed that is required.

It is desirable that the material used for the impact block should be such as not to damage the shuttle tip, should bring the shuttle to rest as rapidly as possible, cause the minimum rebound, have standard physical properties and be economical of material. Of the available materials cast lead appears to satisfy these requirements most completely. Sufficiently soft not to damage the shuttle tip, it brings the shuttle to rest from a speed of 40 f.p.s in about a quarter of an inch with a rebound of about 2 inches By using cast blocks and allowing each face to be struck once only, uniform physical properties are obtained, and there is very little waste of material because the used blocks are readily melted and cast again Some experiments were made with blocks of wood, steel, and brass, but in various ways they were less satisfactory than lead Wood suffers from a lack of uniformity and gives a large rebound, steel damages the shuttle tips, and brass, since it is not readily fusible, leads to a waste of material. With all three substances the extension of the spring was proportional to the shuttle speed, but the constant of proportionality varied with the substance.

The lead block is clamped in position by means of a special clamp adapted to be used with most types of loom, shown diagrammatically in Fig 2 A steel bar A, 8 inches long and of 1 inch square section, is fitted at one end with a projection P which rests against one end of the slot in the base of the shuttle-box. The bar A is held firmly by a rod R, with a cap X at one end and a wing-nut at the other, which passes through a slot in the bar and through the slot in the bottom of the shuttle-box The block of lead B is placed on the box-plate with one face in contact with the end of the bar, and is clamped in this position with a clamp C fixed to the end of the bar. If the shuttle tip is higher than normal the lead block can be raised up by means of thin plates inserted under it so as to bring the centre of the block on a level with the point of the shuttle tip.

The picking at the clamp side is rendered inoperative while an observation is taken and the loom is started from the position where the pick at the side under observation has just finished and the picker has returned to the outer end of the box. This allows the top-shaft to rotate through approximately

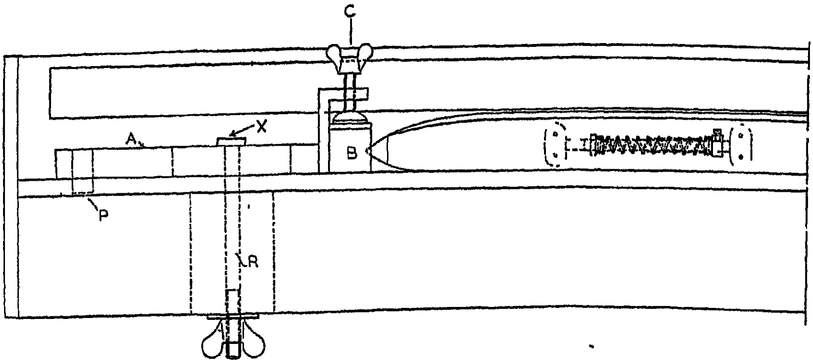


Fig 2
Clamp for Lead Blocks

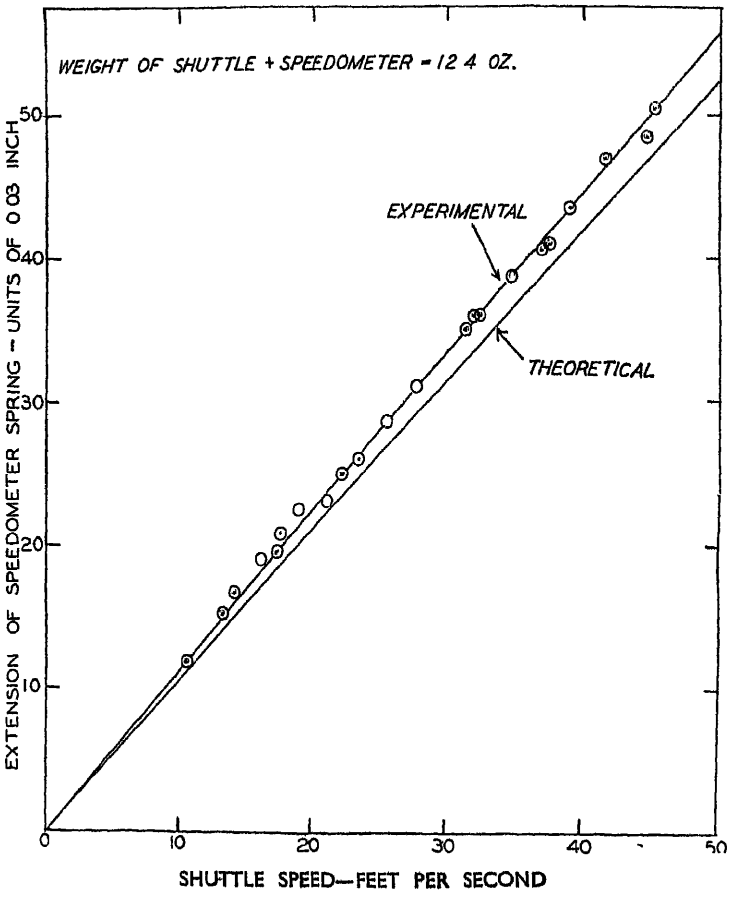


Fig. 3
Relation between Shuttle Speed and Extension of Speedometer Spring

620° before the pick under observation is delivered, and by this time the loom, in all ordinary circumstances, should have reached full speed, observations at mills and the Shirley Institute have not shown the top-shaft of any loom to rotate more than 300° before full speed is reached, whether the looms are driven individually or by countershaft. After each determination the lead block is unclamped and a different face offered to the shuttle until all six faces have been used.

Calibration

Two methods were employed to obtain known shuttle speeds for the purpose of calibration. One was to drop the shuttle from a known height and the other was to measure, by the method described by Thomas and Vincent,[4] the speed of the shuttle just prior to its striking the block. The first method was not convenient for speeds greater than 20 feet per second, corresponding to a fall of about 6 feet, but was used as a check on the second method in the range where the two methods overlapped. The effect of the weight of the collar and spring was negligible. Different shuttle speeds were obtained at the loom by starting the loom in different positions and by varying the length of the picking-band. A typical calibration curve is shown in Fig. 3 where the theoretical line $v = 381e$ (see Appendix) is also shown. It will be seen that with this particular shuttle the extension of the spring for a given shuttle speed is 6·7 per cent. more than the theoretical value.

Effect of the shape of the shuttle tip. For the instrument to be of wide application the calibration should be independent of the shape of the shuttle tip, at least within the range of variation met with in practice That this is so, is shown by the three calibration curves in Fig. 4, which were obtained with the same shuttle fitted in turn with the tips the profiles of which are shown

Effect of the mass of the shuttle. The effect of the mass of the shuttle is shown in Table I. The change in the ratio v/e over the range 10·3 oz. to 12·4 oz. is 4 per cent, so that an instrument calibrated for a mass of 11·3 oz. would be sufficiently accurate for practical purposes over this range and would cover a large proportion of the shuttles used in the cotton industry which, when without the tongue and fitted with the speedometer, lie between the limits stated. For weights outside this range another calibration must be used or a correction must be applied to the existing calibration. The correction factor is readily obtained by dropping the shuttle from a known height and comparing the recorded speed with the speed calculated from the well-known formula $v^2 = 2gh$.

Table I

Mass of shuttle + speedometer (oz)	7·25	10·30	12·40
Ratio v/e (sec.$^{-1}$)	356	373	357

Effect of retardation. Since one important use for the instrument is to measure the speed of impact of the shuttle with the picker, the latter being replaced by the lead block for the purpose of measurement, it is necessary that the instrument be not appreciably affected by the retardation imposed by the swell. To test this point two curves were obtained, shown in Fig. 5. Curve I gives the relation between the diameter of the hole in the lead block, which may be taken as a measure of the shuttle speed at the instant of impact, and the deflection of the speedometer when the shuttle is not retarded prior to striking the block, and curve II gives the corresponding relation when the shuttle suffered retardation by the swell before striking the lead block. In curve II the different readings were obtained from the same unchecked shuttle speed which was retarded by various amounts by varying the swell pressure It will be seen that the two curves do not diverge until the checking is such as to reduce the deflection of the speedometer from 42 to 10 units or less, corresponding to a reduction in speed of 75 per cent or more. Such a swell-pressure

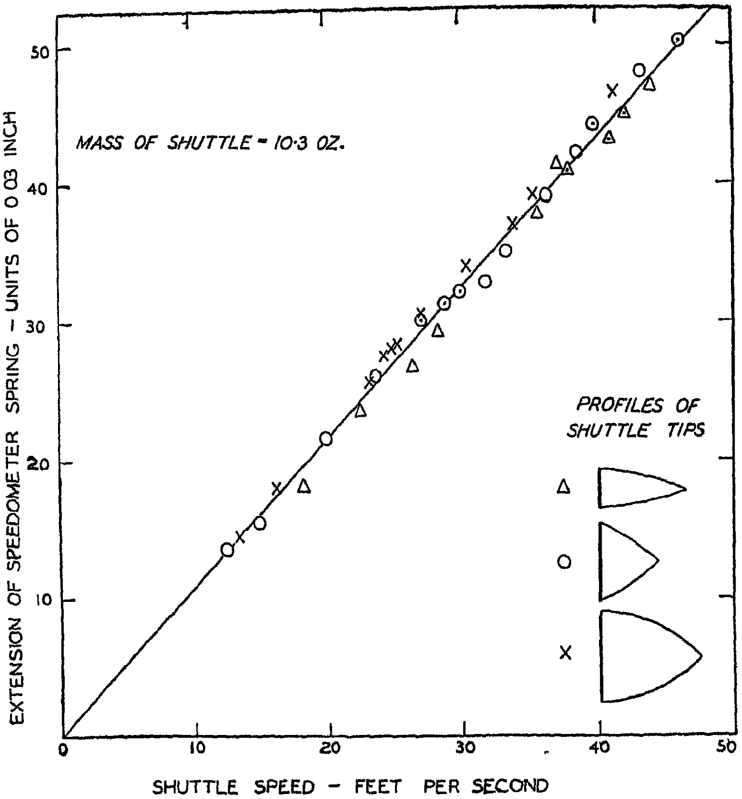


Fig. 4
Extension of Speedometer Spring when the Shuttle is fitted with various Tips.

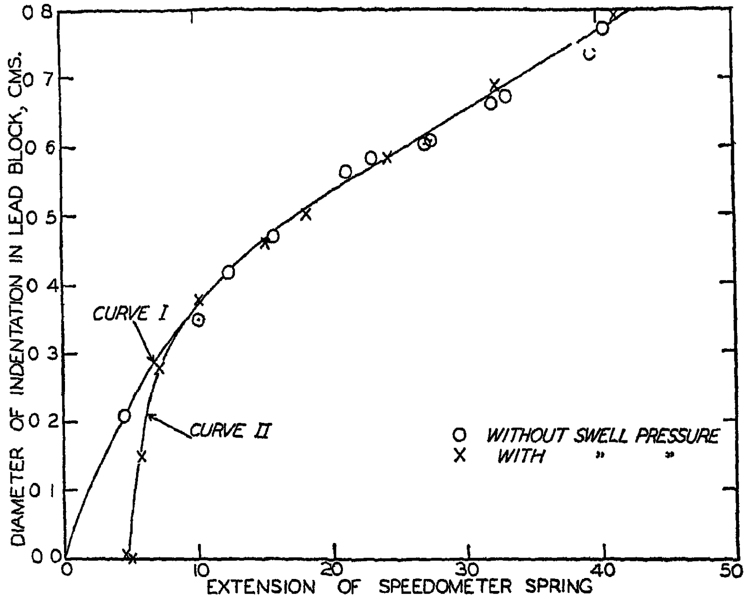


Fig. 5
Relation between the Extension of the Speedometer Spring and the Diameter of the Indentation in the Lead Block

is not often applied in practice, so that on most occasions the instrument can be used with confidence. The diameter of the hole in the lead block was used in this particular instance to measure the speed of impact, but it fails as a general method because of the difficulty of defining accurately the diameter of the hole, which is not perfectly circular, and also because the relation between the diameter of the hole and the speed is affected by the mass of the shuttle and the shape of its tip. Similar remarks apply to the use of the depth of the hole as a measure of the speed of impact.

Accuracy

The deflection of the spring is 0·9 mm. for a speed of 1 foot per second, which allows the instrument to be read to this degree of precision with ease. The rod is marked off in intervals corresponding to 1 foot per second. No error is caused by the friction between the collar and the indicator and the rod unless this friction changes. For this reason the part of the rod on which the collar slides and the inside of the collar should be kept perfectly clean and polished, and should be lubricated with a small quantity of clean spindle oil before taking observations.

Another source of error arises from variation in the lead blocks. The effect of these two sources will vary in a random manner. Their combined effect was tested by dropping the shuttle from a fixed height, corresponding to a speed of 19 f.p.s., forty-three times, using a fresh lead surface each time. The standard deviation of the readings was 1·5 per cent. of the mean. On the assumption that the coefficient of variation is the same as this over the useful range 30-50 f.p.s., the random error of a single reading is unlikely to exceed ± 3·7 per cent. By taking the mean of six readings—a convenient number—when measuring any particular value of the shuttle speed the random error is reduced to a value that is unlikely to exceed ± 1·5 per cent,* and an analysis of the results from which the standard error was determined showed that the value of this error is the same whether all six readings are taken on one block or a number of blocks. Besides this random error, there may be a bias due to faulty calibration of the instrument. This bias arises partly from the above random error and partly from inaccuracy in the measurement of the speed used for calibration, leading to error in determining the correct slope of the line. Provided that about 25 determinations are made for calibrating the instrument it is unlikely that this error will amount to more than 2 per cent. For comparative purposes it is unimportant.

APPENDIX: THEORY OF THE INSTRUMENT

Referring to Fig. 6, let

X be the end of the spring attached to the collar D,
Y be the end of the spring attached to the shuttle through the collar C,
P be the position of X at the instant when the shuttle first meets the lead block,
O be the position of Y at the instant when the shuttle first meets the lead block,
μ be the mass of the operative part of the spring
m be the mass of the collar D with its attached coils,
$M = m + \frac{1}{3}\mu$,
λ = ratio of tension to extension when the spring is extended,
e = the maximum extension of the spring,
$n^2 = \lambda / M$,
v = speed of the shuttle which is required to be measured,
PX = x at time t after shuttle first meets the lead block,
OY = y at time t after the shuttle first meets the lead block,
= some unknown function of t, $F(t)$.

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*The largest likely error is assumed to be 2·5 times the standard error.

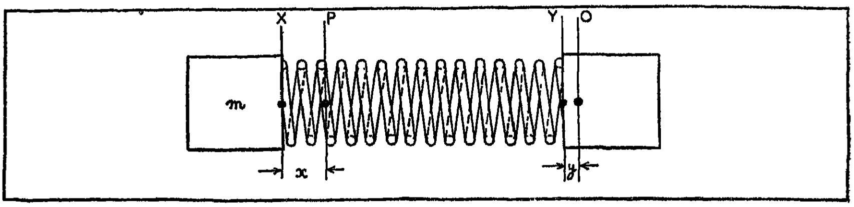

Fig. 6
Diagram illustrating the Displacement of each end of the Speedometer Spring and the Masses attached thereto

Let the shuttle come to rest at time t_1, and let y_1, v_1, and e_1 be the corresponding values of y, $\frac{dx}{dt}$, and the extension of the spring respectively.

Thus y_1 is the depth of the hole in the lead block

Then initially,

$$t=x=y=0 \quad \dots\dots \quad (1)$$

$$\frac{dx}{dt}=F'(t)=v \quad \dots\dots \quad (2)$$

$$\text{At time } t_1,\ F(t_1)=y_1 \quad \dots\dots \quad (3)$$

$$F'(t_1)=0 \quad \dots\dots \quad (4)$$

and at time t the tension in the spring is $\lambda(x-y)$, and the equation of motion is $M\frac{d^2x}{dt^2} = -\lambda(x-y)$ $\dots\dots$ (5)

The mass of the spring is allowed for, as was done by Rayleigh[3] in the analogous problem of the longitudinal oscillation of a mass attached to an elastic rod, by adding one-third the mass of the spring to the value of the attached mass.

Equation (5) may be written

$$\frac{d^2x}{dt^2} + n^2x = n^2F(t) \quad \dots\dots \quad (6)$$

The solution of equation (6) satisfying the conditions (1) and (2) is

$$x = \frac{v\sin nt}{n} + n\sin nt\int_0^t F(t)\cos nt\,dt - n\cos nt\int_0^t F(t)\sin nt\,dt \quad \dots \quad (7)$$

Hence,

$$\begin{aligned} e_1 &= \frac{v\sin nt_1}{n} + n\sin nt_1\int_0^{t_1} F(t)\cos nt\,dt - n\cos nt_1\int_0^{t_1} F(t)\sin nt\,dt - y_1 \\ &= \frac{v\sin nt_1}{n} + n\sin nt_1\left[\frac{y_1\sin nt_1}{n} - \int_0^{t_1}\frac{F'(t)\sin nt\,dt}{n}\right] \\ &\quad - n\cos nt_1\left[\frac{-y_1\cos nt_1}{n} + \int_0^{t_1}\frac{F'(t)\cos nt}{n}\,dt\right] - y_1 \end{aligned}$$

after integrating by parts and using equations (1) and (3), i e

$$e_1 = \frac{v\sin nt_1}{n} - \sin nt_1\int_0^{t_1} F'(t)\sin nt\,dt - \cos nt_1\int_0^{t_1} F'(t)\cos nt\,dt \dots \quad . \quad (8)$$

and by differentiating equation (7)

$$\frac{v_1}{n} = \frac{v\cos nt_1}{n} + n\cos nt_1\int_0^{t_1} F(t)\cos nt\,dt + n\sin nt_1\int_0^{t_1} F(t)\sin nt\,dt$$

$$= \frac{v\cos nt_1}{n} + n\cos nt_1\left[\frac{y_1\sin nt_1}{n} - \int_0^{t_1}\frac{F'(t)\sin nt\,dt}{n}\right]$$

$$+ n\sin nt_1\left[\frac{-y_1\cos nt_1}{n} + \int_0^{t_1}\frac{F'(t)\cos nt\,dt}{n}\right]$$

$$= \frac{v\cos nt_1}{n} - \cos nt_1\int_0^{t_1} F'(t)\sin nt\,dt + \sin nt_1\int_0^{t_1} F'(t)\cos nt\,dt \quad \ldots\ldots\ldots(9)$$

At time t_1, one end of the spring is at rest and the other has a speed v_1. The kinetic energy of the spring is therefore

$$\int_0^l \tfrac{1}{2}\left(\frac{\mu}{l}\right)\left(\frac{z}{l}\right)^2 v_1^2\,dz$$

where l is the strength of the spring at this instant and z is the distance of any point on it from Y, and this integral equals $\frac{1}{6}\mu v_1^2$ Hence the total kinetic energy of the spring and the attached mass at the instant when the shuttle comes to rest is

$$\tfrac{1}{2}\left(\frac{\mu}{3} + m\right)v_1^2 = \tfrac{1}{2}Mv_1^2$$

From this time on, the spring continues to extend until X comes to rest. Assuming that at this instant the whole of the spring is also at rest, then the kinetic energy of the system at time t_1 will all have been transformed into potential energy of the spring, since no external work has been done on the system since Y came to rest, neglecting friction.

Hence $$\tfrac{1}{2}\lambda(e^2 - e_1^2) = \tfrac{1}{2}Mv_1^2$$

$$\text{i.e.}\quad e^2 = e_1^2 + \frac{v_1^2}{n^2}$$

With a spring of adequate extensibility e will be large compared with e_1, and the collar D will not be slowed down appreciably in the period during which the shuttle is brought to rest, so that v_1 differs only slightly from v.

Under these conditions the equation

$$e = \frac{v}{n}$$

is approximately true. A more exact treatment leads to the equation

$$e^2 = \left[\frac{v}{n} - \int_0^{t_1} F'(t)\sin nt\,dt\right]^2 + \left[\int_0^{t_1} F'(t)\cos nt\,dt\right]_0^2 \quad \ldots\ldots\ldots\ldots\ldots(10)$$

from (8) and (9).

Without further knowledge as to the form of $F(t)$ the exact value of e cannot be calculated, but estimates can be obtained in various ways. Two such estimates are given below Although they differ slightly in form, and numerically by about one per cent., they agree in showing that e is directly proportional to v to a very close degree of approximation. This result is of importance in that a linear relation may be used with reasonable confidence when calibrating the instrument from the experimental results.

First estimate.

$$\int_0^{t_1} F'(t)\sin nt\,dt = \sin nt_2\int_0^{t_1}F'(t)\,dt \text{ where } 0<t_2<t_1$$

$$= y_1 \sin nt_2$$

Similarly $\int_0^{t_1} F'(t)\cos nt\,dt = y_1\cos nt_3$ where $0<t_3<t_1$ whence from (10),

$$e^2 = \frac{v^2}{n^2}\left[1 - \frac{2ny_1\sin nt_2}{v} + \frac{n^2y_1^2}{v^2}(\sin^2 nt_2 + \cos^2 nt_3)\right] \quad \dots\dots\dots\dots\dots \text{(11)}$$

The values of t_2 and t_3 are not known but estimates of the right order of magnitude may be made by assuming that each is roughly $\frac{t_1}{2}$, and that $t_1 = \frac{2y_1}{v}$, the value obtained assuming constant retardation. If now n, which within limits can be chosen arbitrarily, is such that $nt_1<0{\cdot}5$, then to a close degree of approximation

$$e^2 = \frac{v^2}{n^2}\left[1 - \frac{2n^2y_1^2}{v^2} + \frac{n^2y_1^2}{v^2}\right]$$

$$= \frac{v^2}{n^2} - y_1^2$$

and $e = \frac{v}{n}\left(1 - \frac{n^2y_1^2}{2v^2}\right)$ approximately.. ....(12)

Now it is found experimentally, as shown in Fig. 7, that y_1, the depth of the hole in the lead block, equals kv approximately, where k is a constant for any particular shuttle; and deviations from this relationship are unimportant since y_1^2 is small compared with v^2/n^2.

$$\therefore\ e = \frac{v}{n}\left(1 - \frac{k^2n^2}{2}\right) \quad \dots\dots\dots\dots\dots \text{(13)}$$

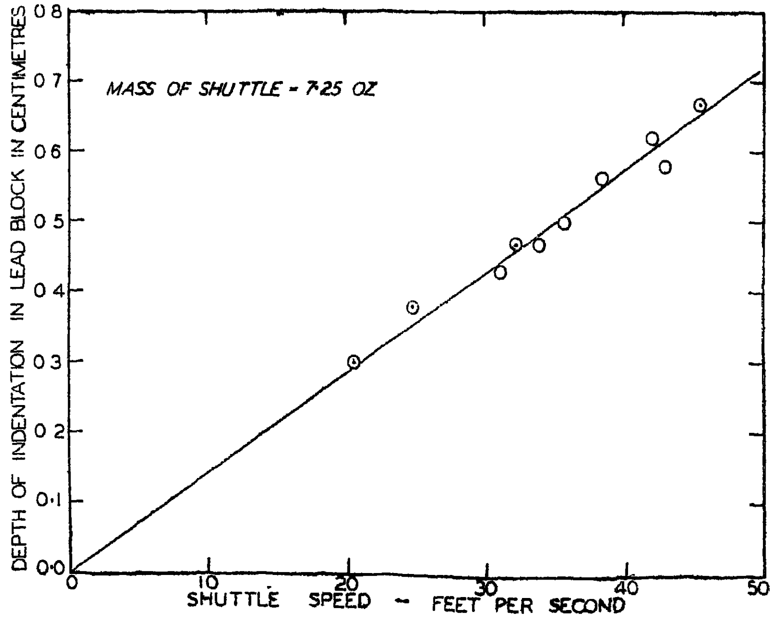

Fig 7

Relation between Shuttle Speed and Depth of Indentation in Lead Block
The speed was measured by the optical method.

Second estimate.

Alternatively, the integrals in equation (10) may be evaluated by making a reasonable estimate of the form $F'(t)$. Since $F''(t)$, which is proportional to the resistance offered to the shuttle, vanishes at $t=0$ and $t=t_1$, an approximate value for $F'(t)$ is

$$\frac{v}{2}\left(1+\cos\frac{\pi t}{t_1}\right),$$

$$\text{whence } F(t)=\frac{v}{2}\left(t+\frac{t_1}{\pi}\sin\frac{\pi t}{t_1}\right)$$

$$\text{and } t_1=\frac{2y_1}{v} \qquad \text{(14)}$$

Substituting the above value of $F'(t)$ in equation (10) we get

$$e^2=\frac{\pi^4 v^2\cos^2\dfrac{nt_1}{2}}{n^2(\pi^2-n^2t_1^2)^2}$$

and

$$e=\frac{\pi^2 v\cos\dfrac{nt_1}{2}}{n(\pi^2-n^2t_1^2)}$$

$$=\frac{\pi^2 v\left(1-\dfrac{n^2t_1^2}{8}\right)}{n(\pi^2-n^2t_1^2)} \text{ approximately}$$

Substituting for t_1 from equation (14) we get

$$e=\frac{v}{n}\left[1-\frac{(\pi^2-8)}{2\pi^2-\dfrac{8n^2y_1^2}{v^2}}\cdot\frac{n^2y_1^2}{v^2}\right]$$

$$=\frac{v}{n}\left[1-\frac{(\pi^2-8)}{2\pi^2-8k^2n^2}\cdot k^2n^2\right]$$

$$=\frac{v}{n}\left[1-\frac{k^2n^2}{11}\right] \text{ approximately} \qquad \text{(15)}$$

The value of n obtained from the mass M and the load extension relation of the spring obtained experimentally, is 380 sec.^{-1}, and the value of k obtained from Fig. 7 is 0.000475 sec., leading to theoretical values of v/e of 386 sec^{-1} by equation (13), and 381 sec^{-1} by equation (15). As already shown the experimental value of this ratio varies somewhat with the mass of the shuttle, a factor of which the theory takes no account, so that the difference between the theoretical and observed values of this ratio will vary with the mass of the shuttle. For a shuttle of mass 10.3 oz. v/e was 2 per cent. less than the value given by equation (15), while for shuttles of 7.25 oz. and 12.4 oz. the experimental value was 6½ per cent less than the theoretical.

Condition that the indicator should record correctly. The indicator will not move further than the sliding collar, provided the friction between the indicator and the rod is capable of causing a greater retardation than the maximum retardation experienced by the sliding collar. The latter retardation occurs when the extension is at a maximum, and is $\dfrac{\lambda e}{M}=n^2e$. If

F is the friction force between the indicator and the rod, and m' is the mass of the indicator, then the retardation due to F is $\frac{F}{m'}$. The condition for correct indication is therefore $F > m'n^2e$, where e is the extension corresponding to the highest speed the instrument is intended to measure. Provided this condition is satisfied F should be as small as possible since it may vary and cause slight errors in the reading hence m' should also be as small as possible.

Acknowledgments. Thanks are due to Mr. E. W Cummings for preparing the drawings of the instrument and to Mr H. B. Williams and his staff for making it.

REFERENCES

[1] Kilgour, R McK., Waring, R , and Boffey, H. *Journal of the Textile Institute*, 1938 T173
[2] Palmer, A , and Ramsdell, F. *Textile World*, 1935, 85.
[3] Rayleigh, Lord " Theory of Sound," second edition, London, 1894, 1, 250
[4] Thomas, I. H , and Vincent, J. J *Memoir* No. XVIII in this series, p 278
[5] Thomas, I H , and Vincent, J J *Loc cit*, p 300

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4—THE ABSORPTION OF THE TWO VAT DYES CALEDON RED BN AND CALEDON JADE GREEN BY COTTON

By A. Geake

Prepared for publication by D. A Clibbens[*]

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This paper describes an investigation of the absorption by scoured cotton yarn of two anthraquinonoid vat dyes from solutions ("vats") of their leuco-compounds prepared, as in normal vat dyeing, by reducing the dyes with sodium hydrosulphite in the presence of sodium hydroxide The dyes were Caledon Jade Green (16:17-dimethoxy-dibenzanthrone, C I. No 1101) and Caledon Red BN (1:2-anthraquinone-naphthacridone, C.I No 1162). The ratio of the weight of cotton dyed to the volume of the dye solution was so small that the absorption of dye by the cotton was accompanied only by an inappreciable fall in the concentration of the dye in solution. The concentration of dye in the dyed cotton was determined by extracting the dye with pyridine, and measuring its concentration in the pyridine extract by spectrophotometric comparison with a standard solution of the dye in the same solvent. The solubility in pyridine of the two dyes used in the work is sufficient to permit this method of analysis, and their solubility in suitable organic solvents is also sufficient to allow them to be purified by crystallization. These were the considerations largely responsible for the choice, from among the vat dyes in common technical use, of these particular representatives

The principal object of the work was to investigate the relation between the composition of the dye solution and the concentration of the dye in the cotton at equilibrium It became evident at an early stage that, although the initial absorption of the dye by the cotton is a very rapid process, the attainment of equilibrium is extremely slow, and the rate is dependent upon the composition of the dyebath, as well as upon the temperature and the conditions of agitation In many cases a strict equilibrium state was not reached within several days, and a critical examination of the results rendered it doubtful whether such a state would be reached by any prolongation of the dyeing within practicable limits The slow attainment of equilibrium is one of the chief difficulties of the work, and, for the critical appraisal of the equilibrium data obtained, it was necessary to make some investigation of the rate of absorption of the dyes by the cotton

The electrolyte content of a vat dyebath is necessarily more complex than that of a direct dyebath since the vat always contains sodium hydroxide and sodium hydrosulphite with the products of its oxidation. In order that the composition of the dye solution shall be constant and defined, the solution must be prepared, and the dyeing process conducted, in the substantial absence of air For reasonable reproducibility in measurements of the rate of dye absorption, the conditions of agitation must be as standard as possible The techniques employed were improved during the course of the work, and the final methods are described in the experimental part, together with other experimental detail necessary for critical appreciation of the work The results obtained are given in the following sections with no more experimental detail than seems necessary for their discussion

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[*] This work was done by the late Dr A Geake during the years 1936-40, and the paper has been compiled from his original notes and reports A study of the effect of the concentration of sodium hydroxide on the absorption of the vat dyes was included in the programme of work, but was not carried out —D A C

The results obtained with Caledon Jade Green will first be described, followed by those obtained with Caledon Red BN. For the early experiments with Caledon Jade Green the sample used, which was described as "B,3000 powder", was kindly provided by Imperial Chemical Industries (Dyestuffs) Ltd. This was a technical preparation free from deliberately added diluents, but not otherwise purified. A large sample of nearly pure 16·17-dimethoxydibenzanthrone became available later, again through the courtesy of Imperial Chemical Industries Ltd., and was used in more critical experiments. The results obtained with the two samples will be described separately. A comparison of the spectrophotometric curves obtained for solutions in pyridine of the technical "B,3000 powder" and of the purified dye showed that the technical sample contained only about 65 per cent. of pure dye. The values of dye concentration calculated from the known weight of technical dye in a given volume were therefore all multiplied by 0·65 in order to render the results more comparable with those obtained in experiments using the purified dye. For all work with Caledon Red BN the commercial undiluted dye (I.C.I.) was first purified by crystallization.

(a) TECHNICAL CALEDON JADE GREEN B,3000 POWDER

In the experiments made with this technical sample of dye, which were the first to be done, dyeing was carried out at 45° C. in an unstirred bath for 2 to 3 days, and the experimental technique was a simple one. The sample of cotton was introduced into the dye solution of the required composition contained in a stoppered flask which it so nearly filled that the available oxygen in the system was negligibly small in relation to the reducing equivalent of the hydrosulphite. The stoppered flask was allowed to stand in a thermostat, the only agitation being an occasional shake by hand. In spite of the long dyeing period the measured absorptions of dye by the cotton may be appreciably below the equilibrium values though there is no precise evidence on this point.

Table I gives the isothermal variation of the dye content *A* of the cotton, expressed in g./100 g., with the concentration *C* of dye in the equilibrium solution expressed in g./100 ml. The solutions were, except in respect to dye content, of identical composition, being 0·1M in sodium hydroxide and 0·006M (0·012N) in sodium hydrosulphite. The temperature of dyeing (45° C.), and the concentration of sodium hydroxide, are approximately those recommended for the commercial dyeing of cotton hanks with Caledon Jade Green. The concentration of hydrosulphite represents a large excess over that required to reduce the maximum amount of dye (pure Caledon Jade Green at 0·01 g./100 ml. is approximately 0·0004N as an oxidant).

Table I

Caledon Jade Green B,3000 powder. Isotherm.

Temperature 45°C., Time 65 hours, NaOH 0·1M, $Na_2S_2O_4$ 0·006M, [Na^+] 0·112M.

Concentration of dye in solution; *C*,g./100ml.	Concentration of dye in cotton, *A*,g./100g	Substantivity ratio, *A/C*	Salt/dye ratio, [Na^+]/*C*
0·000325	0·297	914	345
0·000650	0·455	700	172
0·00163	0·748	460	68·7
0·00325	1·01	312	34·5
0·00650	1·36	209	17·2

The data in Table I are plotted in Fig. 1. As with direct dyes, the concentration of the vat dye in the cotton is seen to rise much less rapidly than its concentration in the solution, or the substantivity ratio falls as the solution becomes more concentrated in dye. The substantivity ratio, which is a measure of the distribution of the dye between the two phases, is defined as the ratio *A/C* between the concentration of dye in the cotton and that in the solution at equilibrium. Its value is included in Table I, where it is seen to fall from about 900 to 200 as the dye concentration in the solution increases from its lowest to its highest value. Fig. 2 shows the logarithmic plot of *A* against *C*, a plot that yields a straight line in those cases where the Freundlich isothermal relation obtains. It is seen that the plot is only approximately linear, the rise in *A* with increasing *C* being slower than is required by the Freundlich equation.

Table II gives the variation of the dye content *A* of the cotton at 45° C. when the concentration of dye in the equilibrium solution was maintained constant (0·0065 g./100 ml.) and the concentration of electrolyte was increased by the addition of sodium sulphate. In these experiments dyeing was continued for 48 hours, again without mechanical agitation, the concentration of sodium hydroxide was constant at 0·05M, and that of the sodium hydrosulphite at 0·006M, whilst the concentration of added sodium sulphate was steadily increased from zero to 0·5M. This is seen to be accompanied by an increase in the substantivity ratio from about 200 to 500. The results are shown in Fig. 3 as a plot of the dye concentration *A* in the cotton against the total electrolyte content of the solution, which is expressed as the total molar concentration of sodium ions $[Na^+]$ and includes a constant and relatively small contribution from the sodium hydroxide and hydrosulphite used in the preparation of the vat. The same data are plotted logarithmically in Fig. 4, the relation then being nearly a linear one. The expression of the results in relation to the total electrolyte content of the solution is a questionable expedient since the effect of the strong base (sodium hydroxide) on the absorption of dye by the cotton is probably different from that of the neutral salt (sodium sulphate). The forms of the curves in Figs. 3 and 4 would, however, be only slightly affected if the concentrations of sodium sulphate were plotted as abscissæ, instead of the total sodium ion concentrations.

Table II

Caledon Jade Green B,3000 powder. Isotherm.

Temperature 45°C., Time 48 hours; Concentration of dye in solution, *C*, *0·0065g./100ml*, NaOH *0·05M*; $Na_2S_2O_4$ *0·006M*.

Concentration of Na_2SO_4, M	Total concentration of sodium ion, $[Na^+]$, M	Concentration of dye in cotton, *A*,g /100g.	Substantivity ratio, *A*/*C*	Salt-dye ratio, $[Na^+]/C$
0	0·062	1·11	171	9·54
0·05	0·162	1·57	242	24·9
0·10	0·262	1·84	283	40·3
0·15	0·362	2·10	323	55·7
0·20	0·462	2·24	345	71·1
0·25	0·562	2·56	394	86·5
0·30	0·662	2·66	409	102
0·40	0·862	3·00	462	133
0·50	1·062	3·35	515	163

The increase in the absorption of dye by the cotton resulting from an increase in the electrolyte content of the solution is presumably due to the same cause as that operating to produce a similar effect with direct dyes. According to a theory of direct dyeing developed recently by Willis, Warwicker, Standing and Urquhart[1] the relation between the substantivity ratio *A*/*C* and the concentration of electrolyte relative to that of dye in the solution (the "Salt/dye ratio," equal to $[Na^+]/C$, when sodium ions are the only cations) should be a unique one, independent of the electrolyte concentration. The results in Tables I and II are shown together in Fig. 5 as a logarithmic plot of *A*/*C* against $[Na^+]/C$, but it is seen that they yield two distinct curves 1 and 2, and that the method fails to co-ordinate the two sets of data. This may be because the concentration of sodium hydroxide was different in the two sets of measurements (0·1, 0·05M), and in this respect data to be given later provide a better test.

Caledon Jade Green B, 3000 powder. Isotherms at 45°C

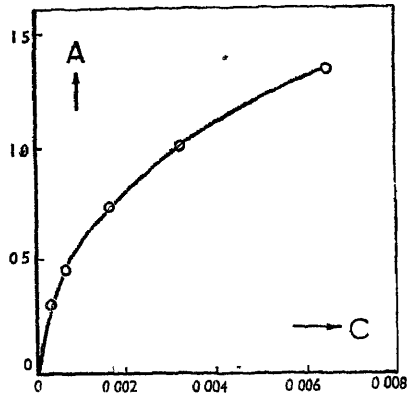

Fig 1.—Variable Dye Concentration in Solution (Table I)

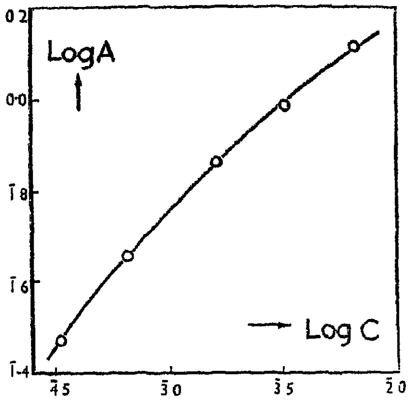

Fig 2.—Variable Dye Concentration in Solution (Table I)

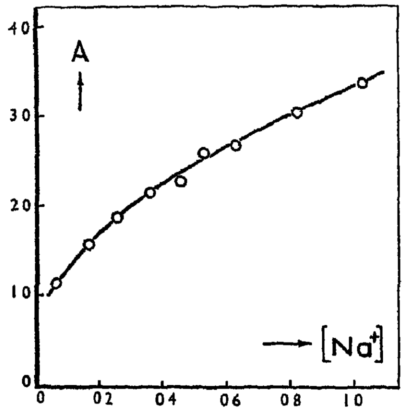

Fig 3.—Variable Electrolyte Concentration in Solution (Table II).

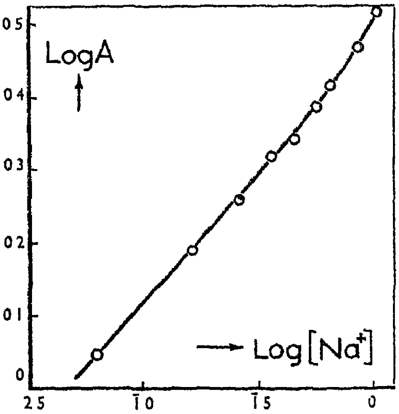

Fig 4.—Variable Electrolyte Concentration in Solution (Table II).

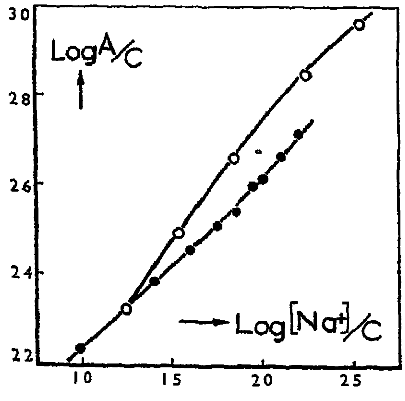

Fig 5.—Variable Dye (o) and Electrolyte (●) Concentrations in Solution (Tables I and II)

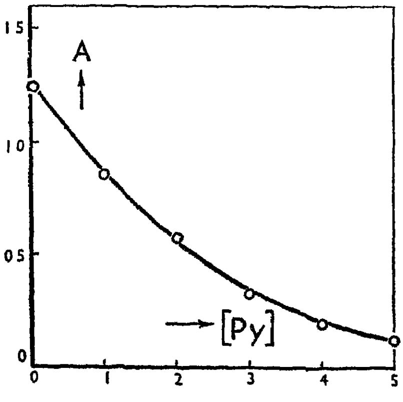

Fig 6.—Variable Pyridine Concentration in Solution (Table III)

Table III gives the variation of the dye content *A* of the cotton when the concentrations of dye in the equilibrium solution (0·0065 g./100 ml.), and of the electrolytes (sodium hydroxide 0·1M, sodium hydrosulphite 0·006M), were maintained constant while pyridine was added in increasing amounts. The effect of pyridine in reducing the absorption of a vat dye by cotton from a solution of its leuco-compound is well known, and Table III shows that the effect is large even when the concentration of pyridine is fairly low; thus the presence of pyridine in the vat at a concentration of 5 per cent by volume reduced the substantivity ratio from about 190 to 20. These results are plotted in Fig 6 for the range of pyridine concentrations up to 5 per cent.

Table III

Caledon Jade Green B,3000 powder. Isotherm.

Temperature 45°C., Time 65 hours; Concentration of dye in solution, *C*, 0·0065g/100ml, NaOH 0·1M, $Na_2S_2O_4$ 0·006M

Concentration of pyridine, [Py], ml./100ml	Concentration of dye in cotton, *A*,g./100g	Substantivity ratio, *A/C*
0	1·24	191
1	0·85	131
2	0·58	89
3	0·33	51
4	0·199	30·6
5	0·131	20·2
7	0·049	7·5
10	0·013	2·0
15	0·003	0·5
20	0·002	0·3

The effect of pyridine is probably due to some kind of association or complex formation between it and the leuco-dye as a result of which the activity of the leuco-dye in the solution is diminished It has been found that the potential of the redox system formed by a solution of the leuco-dye in equilibrium with the solid oxidized form of the dye is raised by the addition of small amounts of pyridine to the system. This also shows that the activity of the leuco-dye (the reductant) is diminished by the presence of the pyridine since the activity of the oxidant should be the same in all solutions that are in equilibrium with the solid oxidized form. Table IV records the potentials E_M of solutions of the leuco-dye of concentration 0·025 g./100 ml. containing various concentrations of pyridine and in equilibrium with the solid oxidized dye. The values given are the mid-point potentials in redox titrations of vats all made up originally to contain double this concentration of dye For these measurements, which were made in a different connection, the purified dye was used, the temperature was 50° C, and the concentration of sodium hydroxide 0·1M; the only other electrolytes in solution were the products of oxidation of the hydrosulphite, which was originally present in slight excess over the vat dye The rise in potential ΔE_M caused by the addition of pyridine to the aqueous vat is plotted in Fig. 7 as a function of the pyridine concentration

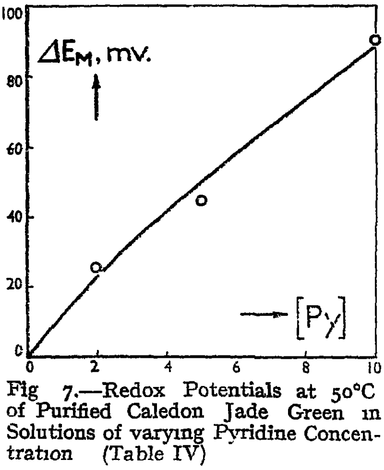

Fig 7.—Redox Potentials at 50°C of Purified Caledon Jade Green in Solutions of varying Pyridine Concentration (Table IV)

Table IV
Purified Caledon Jade Green. Redox Potentials.
Temperature 50°C ; Concentration of dye in solution 0·025g./100ml. ; NaOH 0·1M

Concentration of pyridine, [Py], ml /100 ml	Potential, E_M, mv.	ΔE_M mv.
0	−575	0
2	−549	26
5	−530	45
10	−484	91

If the activity coefficient of the leuco-dye in the dilute aqueous vat free from pyridine is assumed to be unity, and that of the leuco-dye at the same concentration in a vat containing pyridine is denoted by γ, then

$$\Delta E_{\mathrm{M}} = (\mathrm{R}T/n\mathrm{F})\{ln({}^{1}/\gamma)$$

When the temperature of 50° C., the value of n being 2 and potential differences being measured in millivolts, it follows that log γ is equal to $-0{\cdot}0313\Delta E_{\mathrm{M}}$. It is assumed in this calculation that the concentration of semiquinone is negligibly small, an assumption that is probably valid in solutions containing only low concentrations of pyridine.

The activity coefficients of the vats containing pyridine can also be calculated from measurements of the equilibrium absorptions of the dye by cotton, the method being as follows. Let the absorption of dye from a solution containing pyridine in which the dye is at a concentration C be denoted by A. The solution free from pyridine which is in equilibrium at the same temperature with cotton of dye content A contains a lower concentration of dye than C; its actual concentration, which will be denoted by c, can be read from the appropriate isotherm. The activity coefficient of the leuco-dye in the solution containing pyridine is then assumed to be c/C. Activity coefficients for vats containing pyridine have been calculated both from the potential measurements by interpolation on the smoothed curve of Fig. 7, and from the absorption measurements by interpolation on the isotherms of Figs. 1 and 6. They are recorded in Table V, and the

Table V
Caledon Jade Green. Activity Coefficients in Vats containing Pyridine.
Temperature 45°–50°C , NaOH 0·1M

	Potential Measurements		Absorption Measurements	
Concentration of pyridine, [Py], ml./100ml.	Potential rise ; ΔE_M,mv	Activity coefficient, γ	Concentration of dye giving equal absorption in pyridine-free solution ; c,g /100 ml.	Activity coefficient, γ
0	0	1	0·0065	1
1	12	0 42	0 0022	0·34
2	24	0 18	0 0010	0·15
3	34	0 09	0 0004	0·06
4	42	0 05	0·0002	0·03
5	50	0·03	0 0001	0·02

Table VI
Caledon Jade Green. Comparison of Equilibrium Absorptions for different Cottons.
Temperature 45°C ; Time 70 hours ; Concentration of dye in solution 0·0065g./100 ml , NaOH 0 1M , $Na_2S_2O_4$ 0·006M.

Cotton variety —	S. American *Tanguis*	Peruvian *Mitafifi*	Egyptian Uppers	Brazilian	Egyptian Sakel	Arizona *Pima*
Fibre weight, 10^{-8} g./cm. ..	212	202	196	164	149	107
Absorption *A* %	1·34	1·29	1·32	1·32	1·32	1·38

agreement between the values of the activity coefficient obtained by the two independent methods is satisfactory in view of the fairly large observational errors associated with both methods.

Table VI gives the absorptions observed under constant conditions of dyeing (70 hours) for six scoured cottons differing in their country of origin, and consequently in the fineness of the fibre as measured by the fibre weight per unit length. The Table shows that the amounts of dye absorbed by the different cottons are nearly equal, and this fact is some evidence that the absorptions obtained are not far from true equilibrium values since the large differences in fineness of fibre would be expected to influence the rate of dyeing. The equality in the percentage of dye absorbed does not of course mean that all the dyed cottons appeared the same shade; when the dyed samples were arranged in order of increasing depth of shade the sequence was that of increasing coarseness of the staple.

(b) PURIFIED CALEDON JADE GREEN

(16:17 DIMETHOXYDIBENZANTHRONE)

In all the experiments with the purified dye the cotton was agitated in the dye solution. By attachment to a magnetically operated moving support the sample of yarn was thrown up and down in the solution with a reciprocating motion of 150 cycles per minute An apparatus was used in which the dye was vatted, the solution made up of the required composition, and the dye vessel filled, all in an atmosphere of nitrogen In all the experiments the concentration of sodium hydroxide was 0·1M, that of sodium hydrosulphite 0·01M, and hence the total sodium ion concentration 0·12M in the absence of other electrolytes

As a guide to the time required for the attainment of equilibrium the rate of absorption of dye by the cotton was examined under the standardized conditions of agitation. The conditions for, and some of the results obtained in, four experiments on the rate of dyeing are summarized in Table VII. The first three experiments in the Table were all made at 50° C., and the compositions of the equilibrium solutions were altered in such a way that the substantivity ratio varied from about 200 to 2,000. The time required for the absorption to reach half its equilibrium value (Time of Half-dyeing, $t_{1/2}$) is given in the last column. For the three experiments at 50° C., the time of half-dyeing, which is some inverse measure of the rate of dyeing, increases with substantivity ratio, but is relatively short, varying from 4 to 21 minutes. The last experiment in the Table was made at the lower temperature of 25° C. and at a medium value of the substantivity ratio; the much slower rate of dyeing is shown by the higher time of half-dyeing.

Table VII
Purified Caledon Jade Green. Rate of Dyeing.
NaOH, 0·1M; $Na_2S_2O_4$, 0·01M.

Expt. No	Temp. °C.	Composition of dye solution			Equilibrium absorption, *A*%	Substantivity ratio, *A*/*C*	Time of half-dyeing, $t_{1/2}$ minutes
		Dye, *C*, g./100 ml.	Na_2SO_4, M	[Na^+]M			
8	50	0·01	0	0·12	1·71	171	4
18	50	0·001	0	0·12	0·535	535	9
15	50	0·001	0·5	1·12	2·016	2,016	21
13	25	0·0025	0	0·12	1·961	794	70

Purified Caledon Jade Green. Rate of Dyeing

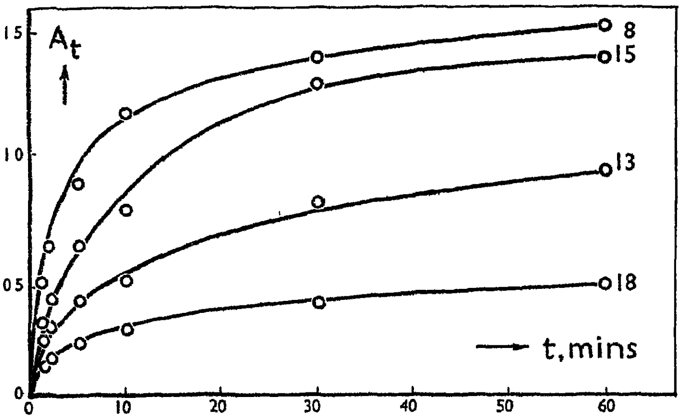

Fig. 8 —Rate in Initial Stages (Tables VII and VIII)

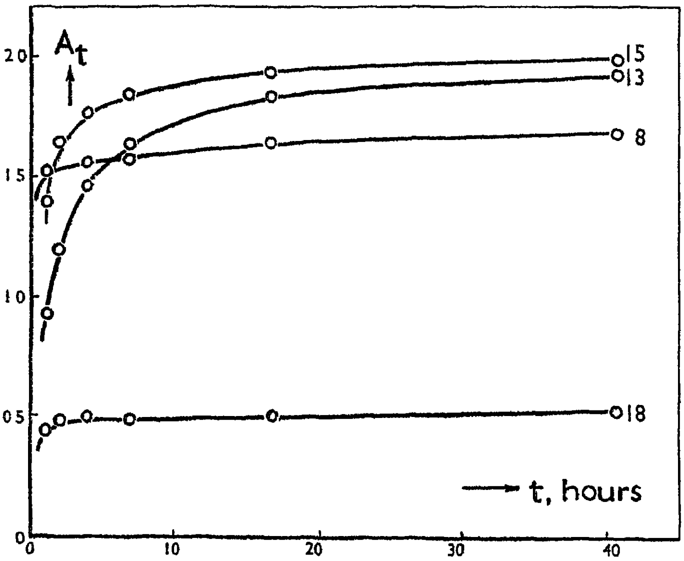

Fig. 9.—Rate in Later Stages (Tables VII and VIII)

The detailed data obtained from the four rate of dyeing experiments are given in Table VIII; the absorptions recorded after 41 hours dyeing have been used as equilibrium values in calculating the time of half-dyeing for Table VII. The absorption A_t at the time t is plotted against the time in Fig 8 for periods up to one hour, and in Fig. 9 for periods between 1 and 41 hours. The striking features of these results are the relatively rapid absorption in the early stages of the process and the relatively slow absorption in the later. During the last 24 hours (between the observations at 17 and 41 hours), the absorption increased by about 2·5 per cent. in the first two experiments, 3·5 per cent. in the third, and 5·5 per cent. in the last. For a process of ideal diffusion (Fick's Law) into an infinite cylinder the time required to reach 99 per cent. of the equilibrium absorption value is about 13 times the time of half-dyeing, namely, periods ranging from about 1 to 15 hours for the half-dyeing times recorded in Table VII. It is clear from Table VIII that the absorption was still increasing at a slow, but experimentally significant, rate in all four experiments after 41 hours. It is also clear that, from the point of view of the attainment of equilibrium, there would be little object in prolonging the dyeing by a day or two; any material improvement in the approach of the end values to the true equilibrium absorptions would necessitate experiments so prolonged as to be prohibitive in any wide programme of work. In the determination of equilibrium isotherms now to be described the dyeing was continued for 41 hours under the standard conditions of agitation, and it was considered that the end values could be regarded as sufficiently close approximations to the equilibrium absorptions.

Table VIII

Purified Caledon Jade Green. Rate of Dyeing.

Time, t		Absorption, A_t, g./100g.			
Hours-Mins		Experiment No 8	Experiment No 18	Experiment No 15	Experiment No. 13
0	1	0·463	0·115	0·291	0·227
0	2	0·637	0·147	0·402	0·277
0	5	0·878	0·210	0·624	0·391
0	10	1·17	0·273	0·771	0·477
0	30	1·41	0·385	1·296	0·806
1	0	1·54	0·448	1·406	0·943
2	0	—	0·487	1·663	1·203
4	0	1·58	0·510	1·789	1·483
7	0	1·59	0·498	1·874	1·651
17	0	1·67	0·523	1·950	1·856
41	0	1·71	0·535	2·016	1·961

Fig 10 shows the isotherms obtained at 25° and 50° C by plotting the concentration of dye in the solution against the absorption of dye by the cotton at equilibrium, the electrolyte concentration being constant (0·1M sodium hydroxide, 0·01M sodium hydrosulphite). The corresponding logarithmic plots of log A against log C are given in Fig. 11, and the experimental data in Tables IX (50° C) and X (25° C.) The isotherm at 50° C. was determined in duplicate, the time allowed for the attainment of equilibrium being 41 and 65 hours in the two experiments; as was to be expected from the investigation of the rate of dyeing, the results obtained for the two different times of dyeing were not appreciably different

Table IX

Purified Caledon Jade Green. Isotherm.

Temperature 50°C , Time 41 or 65 hours , NaOH 0·1M , $Na_2S_2O_4$ 0·01M , [Na^+] 0·12M.

Concentration of dye in solution C, g /100 ml		Concentration of dye in cotton, A, g /100 g	Substantivity ratio, A/C	Salt/dye ratio, [Na^+]/C
41 hours	65 hours			
0·000488		0·350	718	246·0
	0·000492	0·365	741	244·0
0·000990		0·537	542	121·0
	0·000992	0·573	577	121·0
0·00246		0·865	352	48·8
	0·00247	0·831	337	48·8
0·00496		1·20	242	24·2
	0·00496	1·21	244	24·2
0·00996		1·67	168	12·0
	0·00996	1·66	167	12·0

Purified Caledon Jade Green. Isotherms

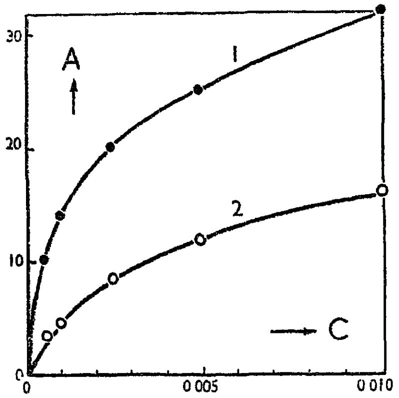

Fig. 10. Variable Dye Concentration in Solution: 1. at 25°C ; 2 at 50°C. (Tables IX and X)

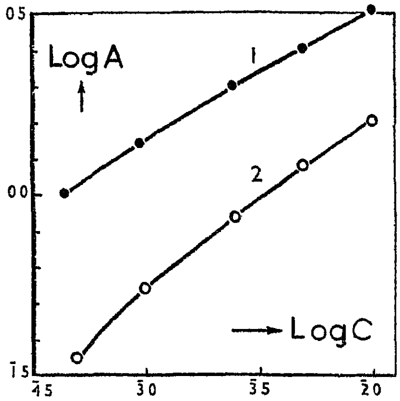

Fig. 11. Variable Dye Concentration in Solution · 1. at 25°C., 2 at 50°C (Tables IX and X)

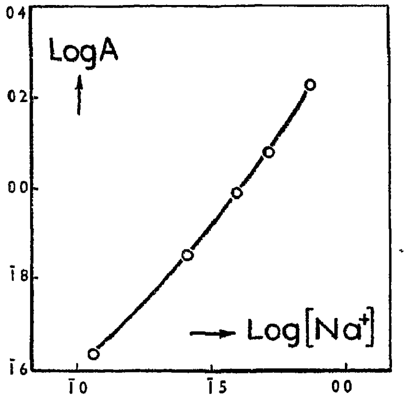

Fig 12.—Variable Electrolyte Concentration in Solution at 50°C (Table XI).

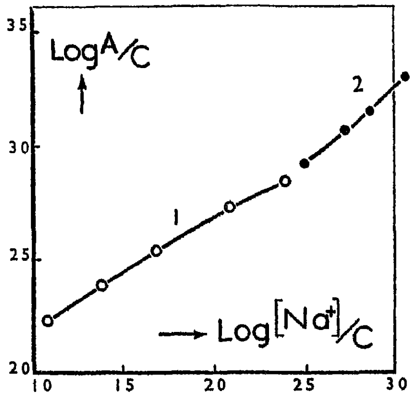

Fig. 13. Variable Dye (1) and Electrolyte (2) Concentrations in Solution at 50° C. (Tables X and XI).

Table X
Purified Caledon Jade Green. Isotherm.

Temperature 25° C.; Time 41 hours, NaOH 0·1M, $Na_2S_2O_4$ 0·01M, [Na^+] 0·12M.

Concentration of dye in solution, *C*, g./100 ml.	Concentration of dye in cotton; *A*, g./100 g.	Substantivity ratio, *A*/*C*	Salt/dye ratio, [Na^+]/*C*
0·000462	1·01	2,183	260·0
0·000967	1·40	1,449	124·0
0·00244	2 01	824	49·2
0·00492	2·55	519	24·4
0·00988	·3·25	329	12·15

The figures show that, as with direct dyes, the absorption of the vat dye from a solution of constant dye content rises as the temperature falls, being roughly twice as great at 25° C. as at 50° C. The logarithmic plots are nearly, but not quite, linear, diverging from the straight in the same direction as that observed with the unpurified dye (Fig 2) and the lines corresponding to the two different temperatures are not parallel. The isotherm obtained at 50° C for the purified dye is almost identical with that obtained at 45° C. for the technical dye (Fig. 1), the compositions of the solutions in respect to electrolytes being practically the same in the two cases. The 45° isotherm would evidently be expected to lie appreciably above the 50° isotherm, and its failure to do so may be due to one or two causes. The technical dye sample contained only 65 per cent. of the pure dye, and although the measured concentrations were corrected accordingly, the 35 per cent. of unknown impurities may have exerted some effect upon the equilibrium. The experiments with the technical dye at 45° C. were also made without mechanical agitation, and the measured absorptions may therefore be further removed on the low side from true equilibrium values than those obtained at 50° C. with the purified dye in a mechanically agitated system.

Table XI contains the experimental data necessary for the construction of an isotherm at 50° C. corresponding to conditions under which the dye concentration in the equilibrium solution was maintained constant (0·001 g./100 ml.) and the electrolyte concentration was steadily increased by the addition of sodium sulphate. Fig. 12 shows these results as a logarithmic plot of the dye absorption, log A, against the total concentration of sodium ions in the solution, log $[Na^+]$ As was found for the technical dye (Fig. 4) the logarithmic relation is nearly linear, diverging from the straight in the opposite direction from that observed for isotherms in which the electrolyte concentration is constant and the dye concentration in the solution variable (Fig. 11). In the present series of experiments the concentration of sodium hydroxide was the same (0·1M) for the isotherms corresponding respectively to constant electrolyte concentration and to constant dye concentration, and the isotherms are shown together in Fig. 13 as a logarithmic plot of the substantivity ratio, log A/C, against the salt-dye ratio, log $[Na^+]/C$. The two sets of data do not in this case overlap, but it is clear that they yield two distinct curves 1 and 2, though this treatment of the results is more nearly successful in co-ordinating the whole of the isothermal data than was the case when the sodium hydroxide concentration was variable (Fig. 5); the failure to obtain a strictly unique relation between substantivity ratio and salt dye ratio could have been predicted from the fact that the curves in Figs. 11 and 12 diverge from the linear in opposite directions.

Table XI

Purified Caledon Jade Green. Isotherm.

Temperature 50°C.; Time 41 hours; Concentration of dye in solution, C, 0·001g./100 ml. NaOH 0·1M; $Na_2S_2O_4$ 0·01M.

Concentration of Na_2SO_4, M	Total concentration of sodium ion $[Na^+]$,M	Concentration of dye in cotton A, g./100g.	Substantivity ratio, A/C	Salt/dye ratio, $[Na^+]/C$
0	0·12	0·533	533	120
0·1	0·32	0·899	899	320
0·2	0·52	1·255	1,255	520
0·3	0·72	1·555	1,555	720
0·5	1·12	2·180	2,180	1,120

All the samples of cotton used in the experiments described were first brought to equilibrium with ("conditioned in") an atmosphere of 60 per cent. relative humidity. Since dyeing is carried out in a dilute aqueous solution it would scarcely be expected that the results would be influenced by the "condition" of the cotton, but this expectation is not entirely justified by experiment. Samples of the same scoured cotton were conditioned for several weeks at 0 per cent. relative humidity (over phosphorus pentoxide), at 60 per cent. (over 74 per cent. glycerol solution), and at 100 per cent. relative humidity (over water). They were then used for rate of dyeing experiments, of which two were made, one (No. 14) at 25° C. and the other (No. 17) at 50° C., the compositions of the dye solutions were so chosen that the equilibrium absorptions at the two temperatures were roughly equal. The results are given in Table XII In each experiment the times at which measurements were made were selected so as to correspond roughly to absorptions equal to 25, 50, 75, and 100 per cent. of the equilibrium values It will be seen that there is no consistent difference between results obtained for the samples conditioned at 0 per cent and 60 per cent relative humidities. But the absorptions by cotton previously conditioned in a moisture-saturated atmosphere were lower than those obtained when the cotton was previously in equilibrium with drier atmospheres, the consistent differences are much too great to be accounted for by any possible experimental error. The last column in the Table gives the percentage differences between the result obtained for cotton conditioned at 100 per cent. relative humidity and the mean result for cotton conditioned in drier atmospheres. It is seen that the effect is greatest at about the time of half-dyeing, but that it remains appreciable at the longest times recorded. No explanation is offered for these observations but, as will be shown, a similar effect is observed in dyeings made from vats of Caledon Red BN It is not possible to say whether the difference is purely one in rate of dyeing, or whether the equilibrium absorptions are also affected, since no truly steady state is reached in the longest times for which observations were made; the direction of the difference is particularly unexpected

Table XII
Purified Caledon Jade Green. Effect of Cotton "Condition" on Rate of Dyeing.

Time t		Absorption, A_t, g./100 g for cotton "conditioned" at				$100\frac{(3)-(4}{(3)}$
Hours	Mins.	(1) 0% R H	(2) 60% R.H	(3) Mean of (1) & (2)	(4) 100% R H.	(3)
EXPERIMENT No. 14 Temperature 25° C , Dye concentration 0·0025g /100 ml						
0	10	0·492	0·491	0·492	0·415	15·6
1	0	0·929	0·912	0·921	0·770	16·4
4	0	1·456	1·424	1·440	1·263	12·3
70	0	2·015	1·992	2·004	1·864	7·0
EXPERIMENT No 17 Temperature 50° C , Dye concentration 0·001 g /100 ml , Na_2SO_4 0·5 M						
0	3	0·463	0·464	0·464	0·403	13·1
0	15	0·874	0·885	0·880	0·734	16·6
1	0	1·409	1·426	1·418	1·247	12·0
17	0	1·985	1·987	1·986	1·876	5·5

(c) PURIFIED CALEDON RED BN
(1:2 ANTHRAQUINONE-NAPHTHACRIDONE)

Caledon Red BN is a "cold dyeing" colour In technical practice it is dyed at the ordinary temperature from a vat containing a lower concentration of sodium hydroxide than that used with the "hot dyeing" colours such as Caledon Jade Green. In most of the experiments described here the temperature of dyeing was 25° C and the concentration of sodium hydroxide in the solution 0·05M The general technique was the same as that used for purified Caledon Jade Green, the cotton sample being agitated in the dye solution under standardized conditions by fixing it to a magnetically operated moving support.

It was observed that the hydrosulphite vat of Caledon Red BN is not strictly stable even in the absence of oxygen. Its spectral absorption curve slowly changes, the maximum of the main absorption band falling and moving towards shorter wave-lengths, the colour change from a bluish red to a more orange shade is readily appreciated by the eye. Nothing is known as to the chemical change involved in this "ageing" of the vat but it is accelerated by an increase in the concentration either of sodium hydroxide or of sodium hydrosulphite in the solution The effect is not due simply to the presence of electrolytes since the rate of change is not affected by the addition of sodium sulphate to the solution When the concentration of sodium hydroxide is 0·5M and that of sodium hydrosulphite 0·1M the ageing is complete in about four days at 25° C, but the vats used in this work (0·05M NaOH, 0·01M $Na_2S_2O_4$) showed no measurable change within a day

Purified Caledon Red BN. Rates of Absorption and Desorption

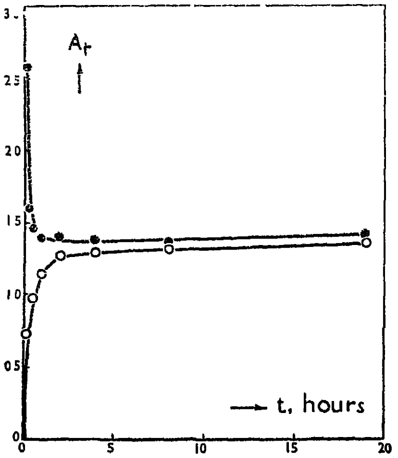

Fig 14.—Temperature 25°C
(Table XIII, Expt 363)

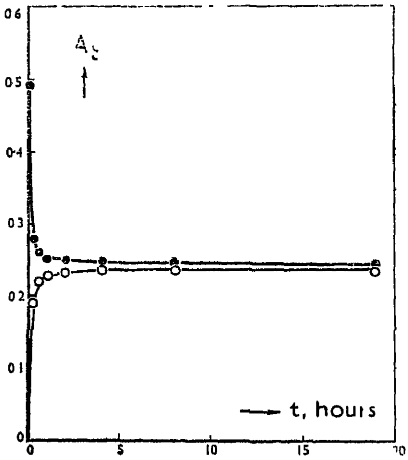

Fig 15.—Temperature 50°C.
(Table XIII, Expt 366)

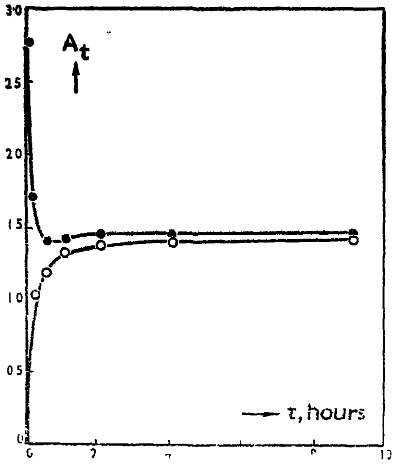

Fig 16.—Temperature 25°C.
(Table XIV)

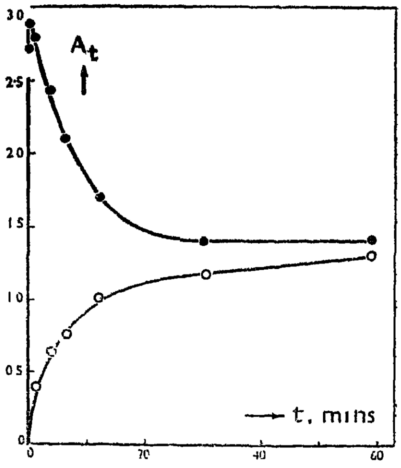

Fig 17.—Temperature 25°C
(Table XIV)

or two The ageing of the vat affects the absorption of the dye by cotton and, even when the concentrations of alkali and hydrosulphite are low, it renders the use of very prolonged periods of dyeing inexpedient in equilibrium studies

In experiments on the dyeing of cotton with Caledon Red BN the equilibrium state was approached from both sides by introducing into the same solution undyed cotton and cotton dyed in such a way as to contain originally about double the content of dye corresponding to the equilibrium state. Dye was thus absorbed by one sample and desorbed from the other, and it was thought that if the dye contents of the absorbing and desorbing samples were nearly equal after a reasonable period of dyeing the mean of the two values might provide the best approximation to the true equilibrium value. Table XIII contains the results of two rate experiments made in this way, one (No 363) at 25° C., and one (No 366) at 50° C. They are shown graphically in Figs. 14 and 15 respectively, where it can be seen that absorption and desorption values in fact approach closely to one another after a few hours.

Table XIII
Purified Caledon Red BN. Rates of Absorption and Desorption.
NaOH 0.05M ; $Na_2S_2O_4$ 0.01M

Experiment 363 Temperature 25° C., Concentration of dye in solution 0·0025 g/100 ml, Na_2SO_4 0·25M Undyed cotton and cotton containing 2·51 g dye/100 g
Experiment 366 Temperature 50° C., Concentration of dye in solution 0·0005 g./100 ml, Na_2SO_4 0·35 M Undyed cotton and cotton containing 0·496 g dye/100 g

Time *t*		Dye content of cotton, A_t, g/100 g			
		Experiment 363		Experiment 366	
Hours	Mins.	Absorbing	Desorbing	Absorbing	Desorbing
0	0	0	2·51	0	0·496
0	12	0·73	1·61	0·192	0·286
0	30	0·98	1·48	0·224	0·264
1	0	1·15	1·41	0·233	0·257
2	0	1·29	1·41	0·239	0·255
4	0	1·31	1·40	0·241	0·255
8	0	1·34	1·38	0·244	0·253
19	0	1·38	1·45	0·247	0·257

An inspection of the data in Table XIII shows, however, that during the last period of observation (8 to 19 hours) the dye content appears to *rise* in the desorbing, as well as in the absorbing, sample. Although the differences that suggest this rise are very small, they may be significant for the following reason. The dyed cotton used for the desorption measurements had been dyed for 22 hours under the general conditions used in this work, that is, with mechanical agitation in a very large relative volume of dye solution. If, however, equilibrium were not attained in this process the dye content of relatively inaccessible parts of the cellulose may have been lower than the equilibrium value for the dye solution into which desorption subsequently occurred. In this case the process would consist of a simultaneous rapid desorption from the more accessible parts and slow absorption by the less accessible parts. After a certain time, the absorption would be the only operative process, and the object of the experiment in fixing more accurately the true equilibrium value would not be achieved. It might be expected that an effect of this kind would be more pronounced if the conditions of dyeing for the sample subsequently to be used in desorption measurements were such as to render the attainment of a true equilibrium state in the initial dyeing process less likely. In an experiment for which the data are given in Table XIV the sample of cotton for desorption was dyed by a normal vat-dyeing process, namely, for 30 minutes at 25° C. in a relatively small volume of solution, that is, with nearly complete exhaustion of the dye liquor. The results of the absorption and desorption measurements for the longer times are shown graphically in Fig. 16, and leave no doubt that during desorption the dye content of the cotton passes through a minimum, and then rises along a curve nearly parallel to the absorption curve.

Table XIV
Purified Caledon Red BN. Rates of Absorption and Desorptio

Temperature 25° C, Concentration of dye in solution 0·025g /100 ml ; NaOH 0·05M, $Na_2S_2O_4$ 0·01M, Na_2SO_4 nil ; Undyed cotton and cotton containing 2·73 g. dye/100 g

Time t	Dye content of cotton, A_t, g /100 g	
	Absorbing	Desorbing
Secs		
0	0	2·730
4	0·164	2·863
16	0·225	2·827
36	0·315	2·753
64	0·390	2·766
100	0·442	2·624
225	0·636	2·417
400	0·753	2·093
Hours Mins		
0 12	1·005	1·703
0 30	1·160	1·377
1 0	1·300	1·400
2 0	1·347	1·418
4 0	1·385	1·422
9 0	1·407	1·455

Table XIV contains some results obtained in this experiment after very short times, and the values for times below one hour are shown graphically in Fig. 17. In the very early stages of the desorption experiment (times of a few seconds) the dye content of the sample is seen first to rise and then to fall. This is due to the fact that when the dyed sample is first introduced into the solution, the dye is wholly in the oxidized form, and the concentration of the leuco-compound in the cotton is zero—as it is in the undyed cotton. Although the reduction of the dye on the cotton by the hydrosulphite in the solution is rapid, it is not sufficiently so to prevent an initial net absorption of dye by the dyed cotton. The shape of the desorption curve is thus complex, and the curve contains both a maximum and a minimum.

The results of the rate measurements show that some compromise is again necessary in selecting the conditions for equilibrium measurements. In the work now to be described the time of dyeing was 20 hours. At times longer than this the rate of change in the dye content of the cotton is very slow, whilst no measurable "ageing" of the vat occurs within 20 hours under the conditions employed. The values obtained must be slightly below the true equilibrium values, but they provide a reasonably accurate picture of the relations in equilibrium systems.

The absorptions of the dye by cotton at 25° C from solutions of variable dye concentration but constant electrolyte concentration are given in Tables XV, XVI and XVII. For all three sets of results the concentrations of sodium hydroxide and sodium hydrosulphite were 0·05M and 0·01M respectively; for the first set (Table XV) no other addition was made to the dye solution, whilst for the second and third sets (Tables XVI and XVII) the dye solution was 0·125M and 0·25M respectively in sodium sulphate. The corresponding isotherms are plotted logarithmically in Fig. 18 where Curve 1 is derived from results obtained in the absence of sodium sulphate, curves 2 and 3 from those obtained with solutions 0·125M and 0·25M respectively in sodium sulphate. The curves diverge slightly, but definitely, from the straight in the direction previously observed for Caledon Jade Green, but they are closely parallel to one another. The effect of adding sodium sulphate to the vat in concentration 0·125M is roughly to double the amount of dye absorbed by the cotton at all concentrations of dye in the solution. The isotherms previously obtained with purified Caledon Jade

Green (Fig. 11, Tables IX and X) are reproduced in broken line in Fig 18, Curve 4 being the isotherm at 25° C., and Curve 5 that at 50° C. for the Jade Green vats in the absence of added sodium sulphate. The isotherm obtained for Caledon Jade Green at 50° C (Curve 5), but not that at 25° C. (Curve 4) is closely parallel to the isotherms for Caledon Red BN at 25° C (Curves, 1, 2, 3) A comparison of Curves 1 and 4 shows that,

Purified Caledon Red BN. Isotherms at 25° C.

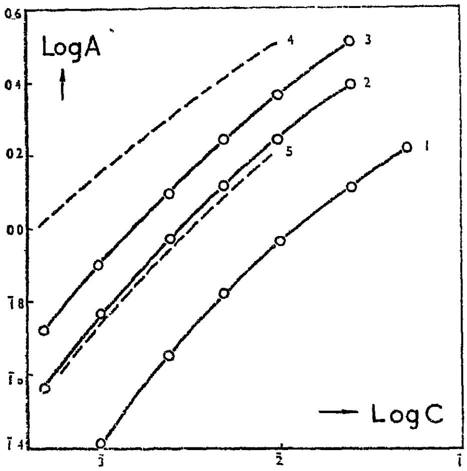

Fig 18—(1), (2), (3) Variable Dye Concentration in Solution. (Tables XV, XVI, XVII). For comparison. Jade Green at 25°C (4) and 50°C (5). (Tables IX and X)

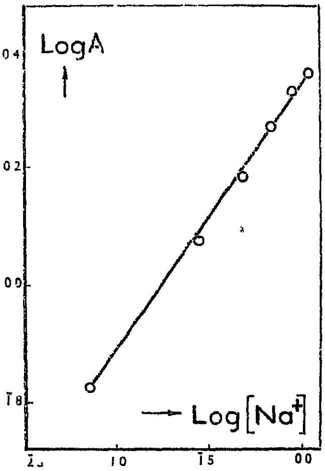

Fig 19 Variable Electrolyte Concentration in Solution. (Table XVIII)

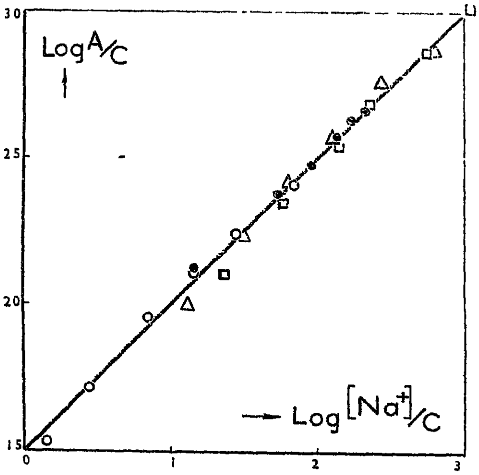

Fig 20—Variable Dye and Electrolyte Concentrations in Solution (Tables XV, XVI, XVII, XVIII).

when the two dyes are dyed at the same temperature (25° C) from vats containing no added salt, Caledon Jade Green is absorbed by cotton in much greater amount than Caledon Red BN, the concentration of the dye in the equilibrium solution (g/100 ml) being the same in the two cases. It is well known that Caledon Jade Green is much more substantive than Caledon Red BN, and this is one of the reasons why the former is a "hot dyeing" the latter a "cold dyeing", colour

Table XV
Purified Caledon Red BN. Isotherm.

Temperature 25° C.; Time 20 hours, NaOH 0 05 M, $Na_2S_2O_4$ 0·01 M, Na_2SO_4 nil, $[Na^+]$ 0 07 M

Concentration of dye in solution, C, g /100 ml	Concentration of dye in cotton, A, g /100 g	Substantivity ratio A/C	Salt/dye ratio $[Na^+]/C$
0 0010	0 26	260	70 0
0 0025	0 45	180	28 0
0 0050	0 67	134	14 0
0 0100	0 92	92	7 00
0 0250	1 30	52	2 80
0 0500	1 68	34	1 40

Table XVI
Purified Caledon Red BN. Isotherm.

Temperature 25° C., Time 20 hours, NaOH 0 05 M, $Na_2S_2O_4$ 0 01 M, Na_2SO_4 0 125 M, $[Na^+]$ 0 32 M.

Concentration of dye in solution, C, g /100 ml	Concentration of dye in cotton, A, g /100 g	Substantivity ratio A/C	Salt/dye ratio $[Na^+]/C$
0 0005	0 37	740	640
0 0010	0 59	590	320
0 0025	0 94	376	128
0 0050	1 32	264	64 0
0 0100	1 75	175	32 0
0 0250	2 49	100	12 8

Table XVII
Purified Caledon Red BN. Isotherm.

Temperature 25° C., Time 20 hours, NaOH 0 05 M, $Na_2S_2O_4$ 0 01 M, Na_2SO_4 0·25 M, $[Na^+]$ 0 57 M.

Concentration of dye in solution, C, g./100 ml	Concentration of dye in cotton, A, g /100 g.	Substantivity ratio A/C	Salt/dye ratio $[Na^+]/C$
0 0005	0 53	1,060	1,140
0 0010	0 79	790	570
0 0025	1 25	500	228
0 0050	1 78	356	114
0 0100	2 31	231	57 0
0 0250	3 25	130	22 8

Table XVIII contains results for the absorption of Caledon Red BN by cotton at 25° C from a solution of constant dye concentration (0 005g./100 ml) and increasing electrolyte concentration obtained by the addition of sodium sulphate to the solution. The results are shown in Fig 19 as a logarithmic plot of the total sodium ion concentration in the solution $[Na^+]$, against the equilibrium concentration of dye in the cotton, A, the logarithmic relation being a linear one within the experimental error.

Fig. 20 shows the whole of the isothermal data for Caledon Red BN, whether at constant dye or electrolyte concentration (Tables XV-XVIII) in a logarithmic plot of the substantivity ratio A/C against the salt/dye ratio $[Na^+]/C$, for all these data the concentration of sodium hydroxide in the solution is constant and equal to 0 05M. The figure shows that an approximate co-ordination of all the data, which cover a thousand-fold range in the salt/dye ratio, can be obtained by this treatment. The whole array of points obtained in this method of plotting lie near to a straight line, though a close inspection shows that individual sets of points describe four distinct and slightly different curves that overlap one another

Table XVIII

Purified Caledon Red BN. Isotherm.

Temperature 25° C , Time 20 hours , NaOH 0·05 M , $Na_2S_2O_4$ 0·01 M , Concentration of dye in solution, *C*, 0·005 g /100 ml

Concentration of Na_2SO_4 M	Total concentration of sodium ion [Na^+] M	Concentration of dye in cotton , *A*, g /100 g.	Substantivity ratio *A*/*C*	Salt/dye ratio [Na^+]/*C*
0	0·07	0·67	134	14·0
0·1	0·27	1·21	242	54
0·2	0·47	1·55	310	94
0·3	0·67	1·89	378	134
0·4	0·87	2·18	436	174
0·5	1·07	2·34	468	214

Table XIX

Purified Caledon Red BN. Redox Potentials.

Temperature 50° C , Concentration of dye in solution 0·0188 g /100 ml , NaOH 0·1 M

Concentration of pyridine , [Py], ml /100 ml	Potential *E*M, mv	Δ*E*M mv
0	−455	0
1·1	−442	13
2·1	−439	16
5·0	−422	33
8·0	−413	42
10·0	−406	49

The effect of the addition of pyridine to the Caledon Red BN vat on the absorption of the leuco-dye by cotton, and its effect on the potential of the redox system formed by a solution of the leuco-dye in equilibrium with the solid oxidized form of the dye, are both qualitatively similar to the effects already recorded for Caledon Jade Green The attempt was again made to compare the effect of pyridine on the activity of the leuco-dye as calculated from potential measurements, with that calculated from measurements of the absorption of the leuco-dye by cellulose On account of the slow establishment of the electrode equilibrium, the potential measurements could not be made with sufficient accuracy at 25° C., and they were therefore made at 50° C. Table XIX gives the potentials at this temperature of solutions of the leuco-dye of concentration 0·0188 g./100 ml. containing various concentrations of pyridine, and in equilibrium with the solid oxidized dye; the concentration of sodium hydroxide in the vat was 0·1M. The rise in potential ΔE_M caused by the addition of pyridine is plotted against the concentration of pyridine in Fig. 21.

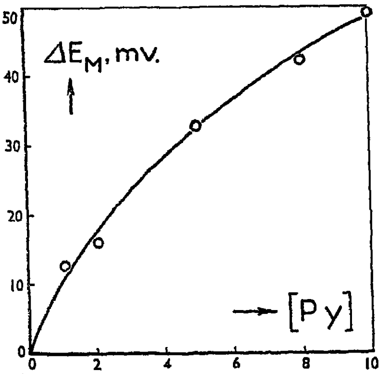

Fig 21.—Redox Potentials at 50°C. of Purified Caledon Red BN in Solutions of varying Pyridine Concentration (Table XIX)

The equilibrium absorptions already reported for Caledon Red BN were all made at 25° C., and a special series of measurements was therefore made at 50° C. for comparison with the potential measurements. In this series a fine-filament viscose rayon yarn was used as the cellulose absorbent for the dye, the time of dyeing was reduced to 4 hours, and the concentration of sodium hydroxide in the vat was 0·1M as in the potential measurements. At the higher temperature, and with the greater concentration of sodium hydroxide, a more prolonged period of dyeing was considered inadvisable in view of the proved instability of the Caledon Red BN vat. The fine-filament rayon yarn was used instead of cotton because this was thought to offer the best chance for the attainment of equilibrium in the relatively short dyeing period. If the effect of the pyridine on the absorption of the dye is due solely to its effect on the activity of the leuco-dye in solution, the relative activities of solutions containing different concentrations of pyridine should, when measured in this way, be independent of the precise nature of the cellulose sample. It is possible that the measured absorptions are appreciably below true equilibrium values, but no great accuracy can in any case be claimed for the comparison of potential, with absorption, measurements. The absorption data are given in Tables XX and XXI corresponding respectively to Figs. 22 and 23. Fig. 22 shows the variation at 50° C. of the equilibrium absorption with the concentration of dye in vats free from pyridine and 0·1M in sodium hydroxide. Fig. 23 shows the variation at the same temperature of the equilibrium absorption with the concentration of pyridine in vats of constant dye concentration (0·025 g./100 ml.) also 0·1M in sodium hydroxide.

Purified Caledon Red BN and Vicose Rayon. Isotherms at 50°C.

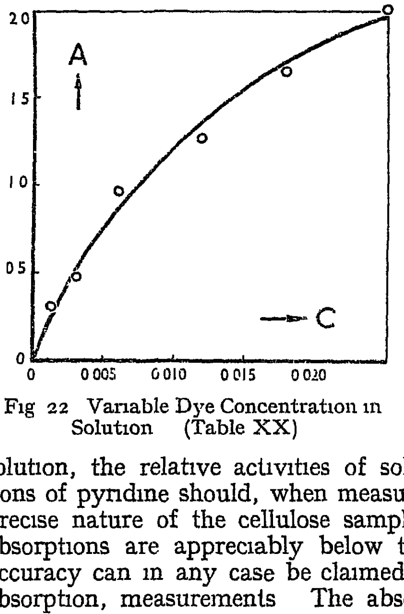

Fig. 22. Variable Dye Concentration in Solution (Table XX)

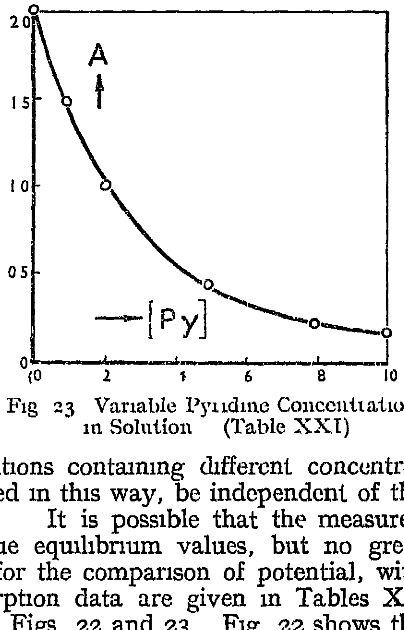

Fig. 23. Variable Pyridine Concentration in Solution (Table XXI)

Table XX

Purified Caledon Red BN. Isotherm (Viscose Rayon).

Temperature 50° C., Time 4 hours, NaOH 0·1 M., $Na_2S_2O_4$ 0·0025 M.

Concentration of dye in solution, *C*, g./100 ml.	Concentration of dye in viscose, *A*, g./100 g.	Substantivity ratio *A/C*
0·0015	0·310	207
0·0032	0·469	147
0·0060	0·965	161
0·0117	1·275	109
0·0180	1·65	92
0·0250	2·02	81

Table XXI

Purified Caledon Red BN. Isotherm (Viscose Rayon).

Temperature 50° C , Time 4 hours , Concentration of dye in solution, *C*, 0 025 g /100 ml , NaOH 0 1 M , $Na_2S_2O_4$ 0 0025 M

Concentration of pyridine [Py], ml /100 ml	Concentration of dye in viscose , *A*, g /100 g	Substantivity ratio, *A*/*C*
0	2 02	81 0
1	1 49	60 0
2	1 00	40 0
5	0 445	17 8
8	0 227	9 1
10	0 164	6 6

As described for Caledon Jade Green, the activity coefficients of the leuco-dye in solutions containing different amounts of pyridine have been calculated from the potential measurements by interpolation in Fig 21, and from absorption measurements by interpolation in Figs. 22 and 23 The two sets of results are compared in Table XXII, which shows reasonable agreement between activity coefficients calculated by the two independent methods

Table XXII

Purified Caledon Red BN. Activity Coefficients in Vats containing Pyridine.

Temperature 50° C , NaOH 0 1 M

Concentration of pyridine , [Py], ml /100 ml	Potential measurements		Absorption measurements	
	Potential rise ΔE_M mv	Activity coefficient γ	Concentration of dye giving equal absorption in pyridine-free solution , *c*, g /100 ml	Activity coefficient γ
0	0	1 0	0 025	1 0
1	10 0	0 49	0 0143	0 57
2	17 0	0 29	0 0075	0 30
3	23 5	0 18	0 0050	0 20
4	28 0	0 13	0 0033	0 13
5	33 0	0 09	0 0024	0 09
8	43 0	0 05	0 0010	0 04
10	48 0	0 03	0 0006	0 025

Table XXIII compares, under constant conditions of dyeing, the absorption of Caledon Red BN by cotton in its normal "condition" (in equilibrium with air at 60 per cent R H) with the absorption by the same cotton previously steeped in water, steeped in dilute sodium hydroxide and hydrochloric acid solutions, and exposed to air saturated with water vapour After treatment with the dilute acid or alkali the cotton was washed with water, but none of the samples was allowed to dry after its pre-treatment and prior to its introduction into the dye solution The results show that all the treatments produced a fall in dye absorption from the value obtained when the cotton was introduced into the dye solution in its normal "condition" The results recorded for samples steeped in dilute sodium hydroxide suggest that the full effect of the wet treatment is only obtained after periods of steeping exceeding one day. These results are similar to those already described in experiments with Caledon Jade Green It is not known whether the effect is due to a change in the equilibrium absorption of the dye, or to a change in the rate of dyeing.

Table XXIII

Purified Caledon Red BN. Effect on Absorption of Pre-treatment of Cotton with Water and dilute Aqueous Solutions.

Temperature 25° C , Time 21 hours , Concentration of dye in solution 0 005 g /100 ml , NaOH 0 05 M , $Na_2S_2O_4$ 0 01 M

Pre-treatment	Concentration of dye in cotton , A, g /100 g		
Brought to equilibrium with air at 60% R H	0 655, 0 651, 0 649 0 654, 0 666, 0 640	Mean	0 653
Steeped in water, 5 days	0 606, 0 604	,,	0 605
,, 6 ,,	0 603, 0 604	,,	0 603
,, 9 ,,	0 601, 0 599	,,	0 600
Exposed to water-saturated air, 6 days	0 594, 0 595	,,	0 595
Steeped in 0 05 M NaOH, 3 hours	0 636, 0 627	,,	0 632
,, 1 day	0 619, 0 611	,,	0 615
Steeped in 0 05 M HCl. 6 days	0 599, 0 592	,,	0 596

EXPERIMENTAL

1. Apparatus and General Procedure

The apparatus and procedure described in this section were used in all experiments with purified Caledon Jade Green and purified Caledon Red BN The vessel in which the dyeing process was carried out is illustrated diagrammatically in Fig 24 It was a cylindrical glass vessel A, designed to contain one litre of solution, closed with a glass lid B, the joint being ground and its tightness ensured by a circular rubber band C drawn over it The narrowed neck of the lid was closed with a rubber stopper D carrying the glass tubes E, F and G. The vessel was filled with solution through the tube F, of narrow bore, whilst the wider tube E served for the evacuation of the vessel or its filling with an inert gas The tube G was a part of the magnetic stirring system, and it enclosed a nickel-plated iron cylinder H supported by a constriction J in the tube G The electromagnet K, surrounding the tube G and resting on the rubber stop L, consisted of about 7,000 turns of 30 SWG copper wire wound on a thin brass former. The samples of cotton yarn to be dyed were supported on the glass framework MPQ suspended by a nickel wire N from the iron cylinder H The electromagnet was controlled through an Isenthal make-and-break switch which interrupted the exciting current 150 times a minute The iron cylinder and the attached glass framework were thereby alternately raised and dropped through about 2½ inches with the same frequency

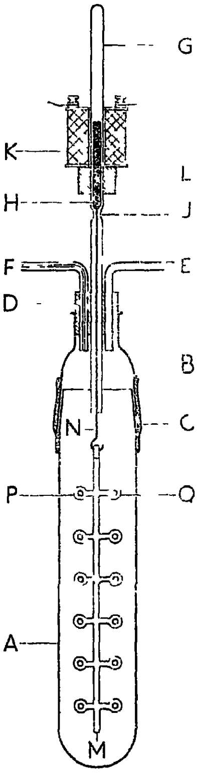

Fig 24
Dye Vessel

The glass yarn-support consisted of a central glass rod M to which were sealed six short glass arms on each side Two opposite arms, such as P and Q, were in the same straight line, and each arm terminated in an eyelet hole The sample of yarn was threaded to and fro alternately through each eye of a horizontal pair of arms, and the yarn ends were finally tied loosely together In this way the yarn was arranged in the form of a loose multi-thread loop, the yarn-support accommodating six such samples, the circumference of the loops was not sufficiently great to permit entanglement between neighbouring samples. A battery of six dye vessels as described, each with its own electromagnet and yarn-support, and submerged in a thermostatically-controlled water-bath, was in use for much of the investigation

The apparatus used for preparing dye solutions of known composition, and for filling the dye-vessels, is shown diagrammatically in Fig. 25. The part A B C was used for the preparation, from a known weight of the dye in its oxidized form, of a solution of the leuco-dye of known composition. This solution, called the concentrated vat, was stored in the litre measuring vessel C, it was much more concentrated in dye than the dye solutions to be prepared from it, but generally of the same concentration in sodium hydroxide and sodium hydrosulphite

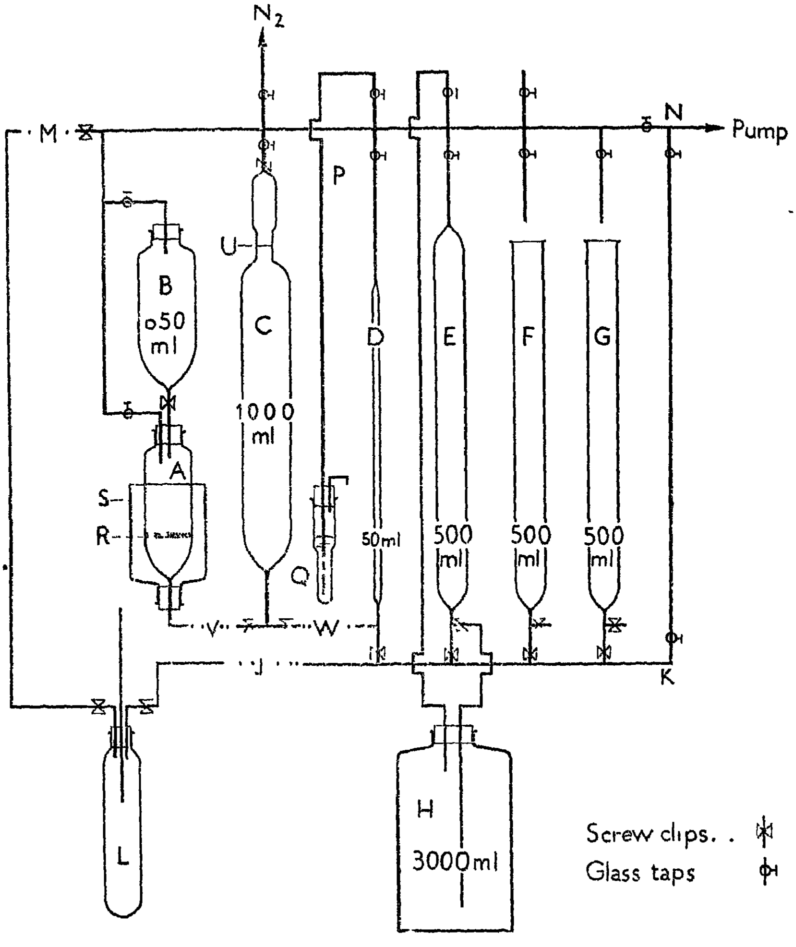

Fig 25 Vatting Apparatus

The part of the apparatus D E F G consisted of a number of burettes for measuring the various solutions to be mixed in order to obtain a dye solution of the required composition and volume The concentrated vat, supplied from the vessel C, was measured from the 50 ml burette D, and the additional alkaline sodium hydrosulphite solution of the desired composition, known as the blank vat, from the 500 ml burette E, which was supplied from the bottle H (3 litres). The two 500 ml. burettes F and G were used for measuring other constituents of the dye solution required to adjust it to a desired composition, for example, water, pyridine or a solution of sodium sulphate of known concentration The four burettes D, E, F, G, were connected at their lower ends to a solution supply-line J K, to which the dye-vessel L could be attached. All parts of the apparatus containing hydrosulphite, with or without the leuco-dye (A, B, C, D, E, H, L) were connected to a gas supply-line MN through which they could be exhausted by means of a Hyvac pump and filled with pure nitrogen. A barometer tube P dipping in a deep mercury well Q was attached to this line. The nitrogen was drawn from a cylinder, freed from oxygen by washing with an alkaline hydrosulphite solution (900 g sodium hydrosulphite, 680 g. potassium hydroxide, 45 g. sodium anthraquinone-2-sulphonate, 5·5 l water), and stored over this same solution in a glass gasholder under a low pressure head. Connections to the gas supply-line were made by sealed glass joints and controlled by ground glass taps, but, for connections to the solution supply-line, rubber tubing joints and screw clips were found more satisfactory with the strongly alkaline solutions. The solution supply-line, and other glass connecting tubes through which solutions passed, were 1·2 mm in internal diameter and residues of solution contained in them could be blown out by nitrogen.

The vessel A contained a sintered glass filter disc R, the diameter of the disc being 5 cm and the capacity above the disc 200 ml , it was surrounded by a glass jacket S The procedure for the preparation of the concentrated vat was the following The weighed amount of purified dye was dissolved, while still in its weighing bottle, in concentrated sulphuric acid, and immediately reprecipitated by pouring the solution into a large volume of water. The precipitated dye was collected on the filter disc R, and for this purpose the vessel A was detached from the rest of the apparatus and supported in an ordinary filter flask, the dye was washed free from acid and left wet with water. The vessel A was then returned to the position shown in Fig. 25 and the connection at V made, but not those at W, M, or J The blank vat to be used for the dissolution of the dye (500 ml) was poured into the vessel B. The concentrations of sodium hydroxide and hydrosulphite were generally double those required in the final dye solution so that when the blank vat was diluted to one litre in the measuring vessel C the concentrations of those components were those desired in the final solution Oxygen was then removed from the vessels A, B and C by alternately evacuating them and filling them with pure nitrogen several times, A and B being finally left filled with nitrogen and C evacuated The blank vat was then run in small portions at a time from B into A, the solution in A being warmed by filling the jacket S with water at about 30° C. (Red BN) or 60° C. (Jade Green) The dye dissolved readily and the solution was drawn through the filter disc into the evacuated measuring vessel C When the whole of the dye had been dissolved the remainder of the blank vat was drawn into C, followed by wash water, and the solution was diluted with water to one litre by filling C to the mark U This procedure ensured that the whole of the dye was reduced, and that the solution contained no particles of undissolved dye The purified dyes were in the form of well-developed crystals, and the vatting of such preparations is a relatively slow process, the success of the procedure outlined above depended upon the use of the dyes in the precipitated form in which they are rapidly reduced and dissolved by alkaline hydrosulphite

The connection at V was finally broken, vessels A and B were removed from the apparatus, and the vessel C was shaken to produce a homogeneous solution This completed the preparation of the concentrated vat

For filling, the dye-vessels (L) were connected in turn to the apparatus at J and M, the yarn-supports having previously been removed They were alternately evacuated and filled with nitrogen several times, finally being left evacuated so that solutions could be drawn into them from the burettes The precise procedure depended upon the nature of the experiment to be made In many of the equilibrium measurements the dye solutions differed in dye concentrations, but were otherwise identical in composition, and contained no constituent other than those required for the vatting. They were then prepared by mixing in different proportions the concentrated vat measured from the burette D, supplied from the vessel C through the connection W, with the blank vat measured from the burette E supplied from the bottle H; the total volume filled into the dye vessel L was generally one litre. When all the required solutions had been added to L, the free space was filled with nitrogen. The two burettes F and G were required when the dye solutions contained an additional variable constituent such as sodium sulphate or pyridine. It was then most convenient to arrange that the concentrated vat and the blank vat together made up a volume of 500 ml of a solution in which the concentrations of dye, sodium hydroxide and sodium hydrosulphite were double those finally desired, the remaining 500 ml was then composed of a mixture in variable proportions of a solution of sodium sulphate, or other addition, and of water, measured from burettes F and G, which required no protection from air. In measurements of the rate of dyeing all the dye solutions in one series of observations were of the same composition The concentrated vat in C was then usually blown with nitrogen into a 5 l measuring flask containing the remainder of the sodium hydroxide and hydrosulphite, and any other constituent The solution was then made up to bulk and drawn into the evacuated dye-vessels, which were finally filled with nitrogen When all the dye-vessels had been filled they were stood in a thermostatically controlled water-bath while the yarn samples were prepared and fixed to the yarn-supports.

The supply of cotton yarn was normally stored over a 74 per cent. glycerol solution in a conditioning chamber at 60 per cent relative humidity The moisture content of the yarn when in equilibrium with this atmosphere was found to be 6 3 per cent , and this value was used in all calculations of dry weights from conditioned weights Since the relative humidity of the conditioning chamber was near to the average relative humidity of the laboratory atmosphere, the conditioned yarn could be weighed, and handled for short periods, in the open air Samples of conditioned yarn of the required length were measured off, weighed, fixed to the yarn-supports as already described, and then returned to the conditioning chamber When the dye-vessels and their contents had reached temperature equilibrium the lids were removed in turn, the yarn-supports with their attached samples were fixed in place on the suspension wires, the vessels again closed, evacuated and filled with nitrogen, and the magnetic agitators set in motion When, in measurements of rate of dyeing, the time of dyeing was 30 minutes or less, the dye-vessels were not again evacuated and filled with nitrogen The procedure then was to remove the lid, fix the yarn-supports to the suspension wires, set the agitators in motion, and plunge the yarn into the dye solution at the zero time

After the dyeing process had been in progress for the desired time, the dye-vessel was opened, the samples were cut from their support, momentarily pressed in a cloth, and each was dropped into a known volume of pure pyridine (10 to 40 ml) contained in a stoppered tube The weight of the tube with its content of pyridine was known, and the weight of wet yarn added to it was determined by weighing the tube again The weight of the dye solution adhering to the yarn, and hence the weight of dye in the adhering solution, could then be calculated This quantity was applied as a correction to the experimentally determined dye absorptions though it was usually almost negligible on account of the high substantivity ratios of the vat dyes

In some experiments cotton yarns previously conditioned at 0 per cent relative humidity (over phosphorus pentoxide), 60 per cent (over 74 per cent glycerol) and 100 per cent relative humidities (over water) were dyed in the same solution and on the same yarn-support A modification of the procedure described above was then necessary The required lengths of yarn were taken from their respective conditioning chambers, and, without weighing, were quickly fixed to the yarn-support, that conditioned at 60 per cent. R.H. first, followed by that conditioned at 100 per cent. R H. and finally that conditioned at 0 per cent. R.H. The yarns were then immediately introduced into the dye solution and dyeing was continued for the requisite time. After the samples had been analysed by extraction of the dye with pyridine the extracted yarn was washed free from pyridine with water, dried and weighed

The total weight of cotton used in any experiment was such that the fall in the dye concentration of the solution due to the absorption of dye by the cotton seldom exceeded 2 per cent and was generally less than 1 per cent.

2. Analysis of the Dyed Yarn

The stoppered tube containing a known volume of pyridine and the sample of dyed yarn was allowed to stand for an hour in a steam oven at a temperature of about 90° C At the end of this time virtually the whole of the dye had been extracted from the cotton and was held in pyridine solution in its fully oxidized form The samples of high dye content still showed a slight colour at the end of the process and remained coloured after more prolonged extraction The small residue of dye could, however, be removed in a second similar extraction process with fresh solvent, but measurements showed that the amount of dye remaining in the cotton after one extraction did not exceed 0·5 per cent of the total dye present, a quantity that could generally be neglected. If the dyed yarn was allowed to dry in the air before being dropped into the pyridine the extraction of the dye from it became much more difficult, and still more so if the drying was completed in a desiccator or an oven

The concentration of dye in the pyridine solution was determined by comparing its optical density, as measured in a photo-electric spectrophotometer, with that of a standard solution of the same dye in pyridine prepared from a sample previously dried to constant weight at 100° C. in vacuo The measurements were made at a wave-length of 655 $m\mu$ for solutions of Caledon Jade Green, and of 503 $m\mu$ for those of Caledon Red BN, these being the wave-lengths of maximum absorption for the two dyes. The standard solutions with which the solutions for analysis were compared contained 6 mg. of purified Caledon Jade Green, or 30 mg of purified Caledon Red BN, in one litre of pure pyridine, the optical density* of both these solutions in a cell 1 cm thick being near to 0·5 at the respective maxima in the spectral absorption curves The volume of pyridine used for the extraction of the dye, and the weights of the cotton samples dyed, were selected so that the concentrations of dye in the pyridine extracts were near to those in the standard comparison solutions. Preliminary work enabled the requisite volumes and weights to be estimated fairly closely, and the concentration of dye in the solution for analysis was generally within 10 per cent of that in the standard solution, if the difference exceeded 20 per cent., a subsidary standard of more appropriate concentration was used in the comparison. The variation of optical density with concentration over this narrow range was represented with ample accuracy by Beer's Law for solutions of both dyes The comparison of two solutions of similar concentration had the further advantage of eliminating a number of possible instrumental errors.

3. Caledon Jade Green

A considerable quantity (about 25g.) of crystalline 16:17-dimethoxydibenzanthrone was provided by Messrs. I.C.I Ltd., and was used in much of the work, under the description "purified Caledon Jade Green" In order to assess the purity of this material small samples were recrystallized once, twice and three times from solution in pyridine (1 g per litre) Its solubility in this solvent is about 0·1 per cent at the boiling point, and the yield of crystals in each crystallization was about 80 per cent. The absorption spectrum in the visible region of the purified Caledon Jade Green after three recrystallizations from pyridine is shown in Fig 26, Curve 1, as a plot of specific extinction coefficient (optical density/concentration in g. per l.) against wave-length. The measurements were made on a solution of the dye in pure pyridine at a concentration of 6 mg per l., and the data from which the curve was constructed are given in Table XXIV The main absorption band has its maximum at a wave-length of 655 mμ, and is characterized on the side of shorter wave-lengths by a slight "hump" in the spectral absorption curve caused by a point of inflection at about 620 mμ The maximum extinction coefficients of the original purified Caledon Jade Green and of the products obtained from it in successive recrystallizations are given in Table XXV. The differences between the values obtained for the products of one, two and three recrystallizations are little greater than the errors of measurement, but the value for the original "purified Caledon Jade Green" is slightly lower than those for the recrystallized products, suggesting that it was not quite free from impurities

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* Optical density= -log Transmittance = log I_0/I, where I is the intensity of light transmitted by the solution, and I_0 that of the light transmitted by the same thickness of solvent

Absorption Spectra of Dyes in Pyridine Solution.

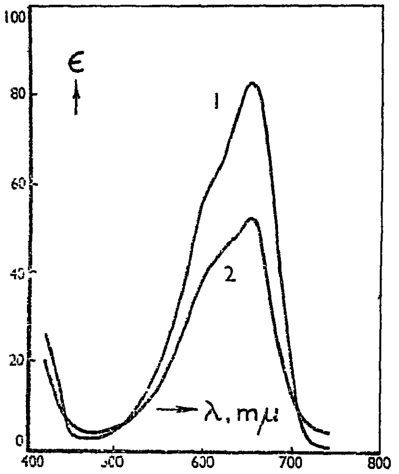

Fig 26 Recrystallized Caledon Jade Green (1), and Caledon Jade Green B, 3000 powder (2)

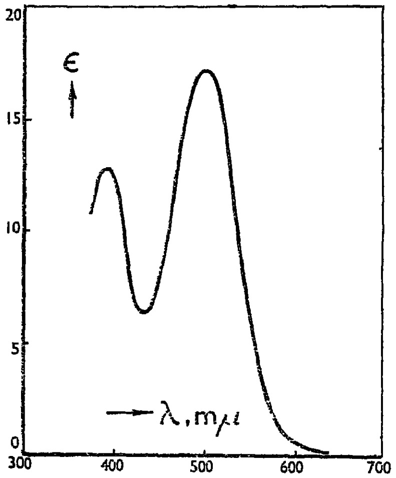

Fig 27 Purified Caledon Red BN (Table XVI)

This was confirmed by the more critical test of a comparison between the spectral curves obtained for the crystals and the various mother liquors The spectrum of the first mother liquor was widely different from that of the recrystallized dye. That of the mother liquor from the second crystallization was much nearer to the spectrum of the crystals; for the third crystallization the spectra of mother liquor and crystals were hardly distinguishable from one another The impurities were substances of relatively higher absorption at wave-lengths outside the main absorption band, namely, at 500 mμ and below, and at 700 mμ and above. No significant differences were observed in the relative absorption at 620 and 655 mμ, and the inflection in the spectral curve at 620 mμ must be regarded as a feature of the pure substance

Table XXIV
Absorption Spectrum in Pyridine of Purified Caledon Jade Green recrystallised three times from Pyridine.

λ = Wave-length, mμ, ε = Specific extinction coefficient = Optical density/concentration, g per l, at concentration 6 mg /l

λ	ε	λ	ε	λ	ε	λ	ε
420	26 2	510	5 6	600	55 8	680	51 1
430	19 1	520	7 4	610	60 4	690	32 9
440	10 0	530	11 0	620	63 8	700	18 2
450	3 9	540	14 2	630	70 0	710	9 6
460	2 4	550	18 6	640	77 7	720	4 7
470	2 0	560	23 5	650	84 0	730	2 2
480	2 4	570	29 4	655	84 0	740	1 2
490	2 9	580	38 0	660	81 9	750	0 8
500	4 0	590	47 6	670	69 6		

Table XXV
Specific Extinction Coefficients at 655 mμ of Purified Caledon Jade Green in Pyridine Solution and of Products obtained from it by successive Recrystallizations.

Material	Extinction coefficient
Purified Caledon Jade Green	81 4
,, recrystallized once	83 6
,, ,, twice	82 6
,, ,, three times	84 0

Caledon Jade Green can also be re-crystallized from nitrobenzene, and its solubility in this solvent at the boil is much greater than in boiling pyridine Hence crystallization from nitrobenzene does not require such an inconveniently large bulk of solvent as is the case when pyridine was used It was found, however, that crystallization from nitrobenzene is less efficient as a method for purifying Caledon Jade Green than crystallization from pyridine. The extinction coefficient of the pure dye in nitrobenzene solution at 655 mμ was, within the errors of measurement, the same as its extinction coefficient in pyridine solution

The above investigation showed that the sample described as "purified Caledon Jade Green," if submitted to no further purification process, probably contained about 3 per cent impurity It was regarded, however, as sufficiently pure for the present purpose, and was used in all the later, more critical, work.

In earlier work a technical material described as Caledon Jade Green B, 3000 powder was used, and its spectral absorption in pyridine solution is given by Curve 2 in Fig 26 The maximum absorption occurs at the same wave-length (655 mμ) as with the recrystallized dye, but the extinction coefficient at this wave-length (52 4) was only about 65 per cent of that of the purified Caledon Jade Green (81 4) or about 63 per cent of that of the purified dye after further recrystallization from pyridine (84 0) In experiments using the technical "3000 powder" the pyridine solution used as a standard in the analysis of the dyed cotton was prepared from the technical dye, and the concentration of the standard solution as determined from the weight of technical dye and the volume of solvent was reduced in the ratio of 1 to 0·65 for the purpose of calculating the results This was done in order to render the results obtained from the technical dye more comparable with those obtained from the purified dye Fig 26 shows, however, that the difference between the technical and pure samples was not entirely one of colourless diluents Relative to the absorption at the maximum, the absorption of the technical sample is obviously higher than that of the pure dye at high and low wave-lengths outside the main band, and at wave-lengths in the neighbourhood of 620 mμ within the band. This is due to the presence of coloured impurities in the technical dye so that a strict comparison of results obtained with the technical and pure materials is not possible even if the colourless diluents in the commercial dye could be regarded as exerting no influence on its absorption by cotton.

4. Caledon Red BN.

The material used in all experiments with this dye was obtained by three successive crystallizations from nitrobenzene of a technical sample described as Caledon Red BN, 900 powder. The first two crystallizations were from 80 volumes of boiling nitrobenzene, the last from 200 volumes of nitrobenzene at 150° C , and the over-all yield of crystals was 64 per cent. The spectral absorption curve of the three-times recrystallized dye, called purified Caledon Red BN in this paper, is shown in Fig 27 as a plot of specific extinction coefficient ϵ against wave-length The corresponding data are given in Table XXVI, and were obtained for a solution of the dye in pyridine of concentration 30 mg /l

The curve is characterized by a principal absorption band with maximum at λ 503, ϵ 17 7, a minimum at λ 435, ϵ 6 5, and a secondary band with maximum at λ 390, ϵ 13 2 The specific extinction coefficients, at the principal maximum and the minimum, of pyridine solutions of the crude dye and of the products obtained in its first, second and third crystallization from nitrobenzene are given in Table XXVII These data show that the third crystallization produced no significant changes in the values

Table XXVI

Absorption Spectrum in Pyridine of Purified Caledon Red BN.

λ = Wave-length, mμ , ε = Specific extinction coefficient = Optical density/ Concentration, g per l at concentration 30mg /l

λ	ε	λ	ε	λ	ε	λ	ε
380	11 5	450	7 75	510	17 2	570	3 45
390	13 2	460	9 9	520	15 8	780	2 05
400	12 6	470	12 6	530	13 4	590	1 15
410	12 1	480	14 9	540	10 7	600	0 7
420	8 05	490	16 8	550	7 9	620	0 3
430	6 7	500	17 6	560	5 3	640	0 1
440	6 6	503	17 7				

Table XXVII

Specific Extinction Coefficients at 503 mμ and 435 mμ of Products obtained by successive Recrystallizations of technical Caledon Red BN, 900 powder

Material	Extinction coefficient	
	503 mμ	435 mμ
Technical dye	15 3	7 4
Do recrystallized once	17 1	6 4
Do do twice	17 6	6 4
Do do three times	17 7	6 5

In work incidental to this investigation the absorption spectrum of purified Caledon Red BN was measured, not only in pyridine solution, but also in concentrated (94 per cent) sulphuric acid solution, and in a solvent composed of 30 volumes of concentrated sulphuric acid with 70 volumes of glacial acetic acid The spectrum of the leuco-dye (vat) was also measured in solutions for which the concentration of sodium hydroxide varied from 0·05 to 0 5M, of sodium hydrosulphite from 0·01 to 0 1M, and of sodium sulphate from 0 to 0 4M. The spectrum of a vat buffered at *pH*9 by the addition of boric acid in appropriate quantity to a caustic vat was measured, as well as that of a vat made acid by the addition of acetic acid in slight excess of the sodium hydroxide present in a normal vat. In all these cases measurements were made on freshly prepared solutions of such a concentration in dye that the maximum optical density was near to 0·5 in a cell 1 cm. thick. All the solutions, whether of oxidized or reduced dye, gave spectral curves characterized by a principal, symmetrical and fairly sharp, absorption band. Some of the data obtained from these curves are collected in Table XXVIII.

Table XXVIII
Spectral Data for various Solutions of Purified Caledon Red BN.
λ = Wave-length, mμ, ε = Specific extinction coefficient

Solution	Band maximum λ	ε	Band width at half height, mμ
Oxidized form			
in Pyridine	503	17·7	89
,, 94% H_2SO_4	460	32·1	114
,, 30 vol H_2SO_4 (94%) 70 vol Acetic Acid)	430	34·2	90
Reduced form			
Vat, NaOH 0·05–0·5M, $Na_2S_2O_4$ 0·01–0·1M, Na_2SO_4 0–0·4M	525	42·8	135
Vat, *pH*9 .	460	42·0	100
Vat, acid . .	430	27·7	115

For solutions of Caledon Red BN in concentrated sulphuric acid, and in the mixture of concentrated sulphuric and anhydrous acetic acids, the bands are sharper, the maximum extinction coefficients much higher and at shorter wave-lengths, than for solutions in pyridine. The general procedure used for the preparation of vats in this investigation involved dissolving the crystalline dye in concentrated sulphuric and reprecipitating it with water. It seemed desirable to establish the absence of any serious decomposition of the acridone on treatment with concentrated sulphuric acid, and it was primarily for this purpose that the spectrum of Caledon Red BN in sulphuric acid was examined. The optical density of the solution at the maximum in the absorption band was measured repeatedly at intervals over a period of several hours following the preparation of the solution. It was observed to fall linearly with time at the approximate rate of 0·5 per cent. per hour. Since, during the procedure outlined for the preparation of the vat, the dye is in contact with concentrated sulphuric acid only for about 15 minutes, it was felt that no serious decomposition could occur under the conditions employed.

Spectral measurements on solutions of the leuco-dye were made primarily with the object of examining the stability of the vat. Variations in the concentration of sodium hydroxide, sodium hydrosulphite and sodium sulphate within the wide limits given in Table XXVIII were without influence on the spectrum of the vat; these measurements were all made on solutions containing 12·5 mg. Caledon Red BN per litre. A reduction in *pH* of the vat to a value of 9 caused a shift in principal absorption band in the direction of shorter wave-lengths. A still greater shift in the same direction occurred when the vat was made slightly acid, and was then accompanied by a large fall in extinction coefficient, measurements made on the acid vat were not very accurate on account of a gradual clouding of the solution caused by decomposition of the hydrosulphite. The change in the spectrum of the vat caused by a decrease in its *pH* was no doubt due to the formation of less highly ionized forms of the leuco-dye (anthrahydroquinone).

The bluish-red Caledon Red BN vats containing high concentrations of sodium hydroxide become more orange in colour when stored for some time, and this effect is still more pronounced when the concentration of hydrosulphite is also high. The wave-length of maximum absorption falls from 525 mμ to 480 mμ and the specific extinction coefficient from 42·7 to 39. The process responsible for this change has been called the ageing of the vat. It occurs when the vat is preserved under an atmosphere of pure nitrogen, and its effects on the spectrum is not unlike that produced by a fall in *pH* (Table XXVIII), though no change in *pH* occurs during ageing. The ageing of a vat 0·5M in sodium hydroxide, 0·1M in sodium hydrosulphite, containing 60 mg. Caledon Red BN per l., and stored under nitrogen, was complete in about four days at 25° C.; it obeyed the monomolecular rate-law within the experimental errors. The spectral curves obtained after various shorter times of storage possessed a common point of intersection (isobestic point) at λ 490 mμ, ϵ 37·7, so that at intermediate times the solutions contained a simple mixture of an initial and end product. There was no significant change after one day's storage at 25° C. in the spectrum of a vat 0·05M in sodium hydroxide and 0·01M in sodium hydrosulphite, these being the concentrations generally present in the dye solutions used in this investigation, extrapolation from results obtained at higher concentrations of alkali and hydrosulphite suggest that the rate of change under these conditions would be about 1 per cent. per day.

When fully aged vats were completely oxidized with air the initial amount of Caledon Red BN was recovered quantitatively, and the spectrum of the recovered dye in pyridine solution was unchanged, but the colour change occurring in the ageing vat—from bluish-red to orange—was not reversed by slow oxidation with air. The ageing process is not simply an effect of electrolytes, and is not produced by high concentrations of sodium sulphate. It may be due to a reduction of the dye beyond the normal stage, but there is no evidence on this point.

Cotton absorbed less dye from an aged, than from a normal, vat, and when measurements of dye absorption are to be made vats cannot safely be kept more than a day or two even when the concentrations of sodium hydroxide and hydrosulphite are as low as 0·05M and 0·01M respectively, at higher concentrations serious changes may occur in a day.

5. Other Detail

A soft-twisted, two-fold, cotton hosiery yarn, made from Egyptian cotton spun and doubled to a count of 40s/2, was used in most of the work. It had been scoured by boiling for several hours with 1 per cent. sodium hydroxide solution at an excess pressure of 20 to 30 lb./sq. in., and had then been washed successively with water, dilute acid and water. The yarn was air-dried and conditioned at 60 per cent. relative humidity over a 74 per cent. glycerol solution.

In one series of experiments (Table VI) a comparison was made between the absorptions of dye by a number of yarns made from different growths of cotton. These yarns were all of the same construction as that given above, and had all been scoured in a similar way. In another series of experiments made for a special purpose (Tables XX, XXI) the absorbent was a scoured viscose rayon yarn, 100 denier with 100 filaments.

Measurements of optical density, and spectral absorption measurements, were made with a photo-electric spectrophotometer designed and made in these laboratories. The absorption cells were 1 cm. thick, those used for solutions that could not be exposed for long to the air (vats and solutions in concentrated sulphuric acid) being cylindrical and closed with ground glass stoppers. The performance of the whole apparatus was checked frequently. Redox potentials were measured in potentiometric titrations of the vats against a standard oxidizing solution substantially as described by Geake and Lemon[2]

SUMMARY

The paper describes an experimental study of the equilibrium absorption by scoured cotton of Caledon Jade Green (16 17-dimethoxydibenzanthrone) and of Caledon Red BN (1 2-anthraquinone-naphthacridone) from alkaline solutions of their leuco-compounds (vats) Some results are also given on the rate of absorption of the leuco-dyes by cotton from their vats The chief variables considered are the concentrations of dye and of neutral electrolyte in solutions of constant concentration in sodium hydroxide. The effect of pyridine in diminishing the absorption of the dyes by cellulose is correlated with its effect in raising the redox potential of the system formed by the solution of the leuco-dye in equilibrium with the solid oxidized form The rate of dyeing, and possibly the equilibrium absorption, are shown to be diminished if, before dyeing, the cotton is soaked in water or dilute aqueous solutions, and not dried prior to dyeing
soaked in water or dilute aqueous solutions, and not dried prior to dyeing
The special apparatus and technique designed to give maximum accuracy in the measurements are described, and a number of data on the spectral absorptions of solutions of the purified dyes in various solvents are recorded.

REFERENCES

[1] Willis, Warwicker, Standing and Urquhart *Shirley Inst Mem*, 1944-45, 19, 223, or *Trans. Faraday Soc*, 1945, 41, 506

[2] Geake and Lemon *Shirley Inst Mem*, 1937-38, 16, 125, or *Trans Faraday Soc*, 1938, 34, 1409

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TRANSACTIONS

5—THE USE OF A TRELLIS MODEL IN THE MECHANICS OF HOMOGENEOUS MATERIALS

By K Weissenberg

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INTRODUCTION AND SUMMARY

Materials in general behave in a very complex manner when subjected to mechanical actions, which may occur in the various stages of manufacture, in experimental tests, and in practical use To unravel the complexities various attempts have been made on two distinct scales, a macroscopic one in which the materials appear as continuous media, and a microscopic one in which the apparent continuity of the materials is resolved into a discontinuity with a more or less coarse grain according to the crystalline, colloidal, molecular and atomic structure For these attempts the classical theory of mechanics developed a mathematical formalism which has been greatly simplified by the introduction of a mechanical model, which is referred to as a *trellis*, since it behaves like the well-known type of collapsible garden trellis, consisting of two intersecting series of parallel rigid rods, pinpointed to one another where they cross, and capable of extending and contracting in certain directions without a change in the length or the form of the rods *

In the present paper a comprehensive scheme is developed in which the classical theory and the theory of the trellis model are united to account for the behaviour of materials under mechanical actions. The scheme starts by considering an *ideal medium,* defined as a three-dimensional continuity of individually recognisable material points, or *mass-points* for short, and assumes that the freedom of movement of the ideal medium is restricted so that from all conceivable movements only those can occur which are in agreement with the fundamental laws of the classical theories of the mechanics of continuous media, that is with the law of *preservation of continuity,* the law of a *dynamical equilibrium of the forces,* and the law expressed as an *equation of state* which relates the stresses and strains and their time derivatives at any point in the material According to Lagrange it is possible to visualise all restrictions to the freedom of movement as *forces of restraint* which act between otherwise freely movable mass-points, and when these Lagrange forces of restraint are calculated for the various laws of the classical theory it is found that they can be incorporated in a trellis mechanism which guides the mass-points along the movements allowed by the laws, and prevents the mass-points from executing movements along any other way Thus the theory in a trellis mechanism is developed in which the trellis becomes a model for the ideal medium The combined theories of the classical mechanics and of the trellis model are then applied to any given real material by intervention of statistical considerations in which the coordinates and forces of the ideal medium are defined as appropriate statistical means of the coordinates and forces of the mass-points of the real material

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* A trellis of this kind was already used in an earlier investigation, see K Weissenberg, "La Méchanique des Corps Déformables," *Arch d Sci et Nat*, 1935, 5me Por, Vol 17

In the theory of the trellis model one may consider first a hypothetical continuum of freely movable mass-points, and divide it into cells by mutually intersecting curves and surfaces, the division being chosen sufficiently fine to give differential cells, that is cells of infinitesimally small dimensions Each differential cell, however small, will still contain an infinitely large number, N say, of individual mass-points, and will accordingly have an infinitely large number, $3N$, of degrees of freedom in an arbitrary change from some *initial* to some *terminal position*. Subjecting, then, the continuum to the laws of the classical theory one obtains an ideal medium in which the freedom of movement is restrained The first of the classical laws, dealing with the preservation of continuity, postulates that in an arbitrary change from an initial to a terminal position the medium suffers a *strain* such that for the continuum of mass-points the three components of the displacement vector are continuous and regular * functions of the space coordinates of the mass-points When the medium is again arbitrarily divided into cells it follows from the continuity and regularity of the functions that by making the cell division finer and finer one reaches a stage in which each cell demarks a region of *homogeneous strain*, that is a region in which the functions approach to linear forms of the coordinates with any desired degree of accuracy The regions of homogeneous strain may contain one or more differential cells but, however large or small they are, they can have only *twelve degrees of freedom of movement* in accordance with the twelve constants which specify a general linear transformation of coordinates The law of preservation of continuity therefore imposes a restraint on the mass-points in every differential cell such that from the infinitely large number, $3N$, of degrees of freedom only twelve are *allowed* while $3N$-12 are *forbidden*, and the law is thus equivalent to the assumption of Lagrange forces of restraint, which resist infinitely strongly a movement along a forbidden degree of freedom, and offer zero resistance again at a movement along an allowed degree To find explicitly the allowed and forbidden degrees of freedom, and the Lagrange forces of restraint associated with them, it is necessary to recall the invariants implied by the law since the allowed degrees of freedom will correspond to movements in which the invariants are maintained while the forbidden ones will correspond to movements in which the invariants would change It will be remembered from the classical theory that the law implies amongst others, two invariants† One of these is of a universal character and expressed in the form that—according to the law—any two intersecting curves or surfaces imprinted in the medium cannot glide over one another but maintain all *points of intersection* intact and *invariant* throughout all changes in position as if the curves and surfaces were *pinpointed* to one another where they cross The other invariant is of a more specific character and must be expressed separately for each region of homogeneous strain, and for each ordered pair of initial and terminal positions Within a region of homogeneous strain the translation from an initial to a terminal position involves changes in length which are so distributed over the full solid angle of directions that at every mass-point a certain surface of second degree, termed *strain ellipsoid*, changes its form from a sphere in the initial position to an ellipsoid in the terminal position, while another surface of second degree, termed *reciprocal strain ellipsoid,* changes its form conversely from an ellipsoid into a unit sphere. Both the strain ellipsoid and the reciprocal strain ellipsoid are centred on the same mass-point and determine by their common centre and by their lines of intersection in either position, a conical surface of second degree, termed *cone of zero elongation* The generating lines of the cone, termed *lines of zero elongation,* are invariants in the sense that they can change only in orientation but have the same length, the same straight linear form, and the same points of intersection both in the initial and terminal position. In the interior of a region of homogeneous strain the lines of zero elongation have the same directions at all mass-points, but the directions change in general when one proceeds from one such region to another Taking, then, each region of homogeneous strain in turn, and constructing there the lines of zero elongation, one may arbitrarily select in each region three such lines (not coplanar) and imprint throughout the whole medium a pattern of three mutually intersecting families of lines of zero elongation, respectively parallel to the three chosen lines, and drawn sufficiently close so that each region is subdivided into a large number of differential cells of infinitesimally small dimensions. All the lines in the pattern are in each region of homogeneous strain invariants with regard to length, straight linear form and points of intersection, and this invariance permits a separation of the degrees of freedom into allowed and forbidden ones, and an explicit determination of the Lagrange forces of restraint involved The degrees of freedom, allowed by the law, and accordingly resisted by zero forces of restraint, correspond to movements in which the lines of the pattern change only their orientations in space, while the degrees of freedom forbidden by the law, and accordingly resisted by infinitely strong forces of restraint, correspond to movements in which the lines of the pattern contained in any one region of homogeneous strain change their length, their straight linear form, or their points of intersection All these forces of restraint can be incorporated into a mechanism which is deduced from the pattern by replacing separately in each region of homogeneous strain the lines of the pattern by straight rigid rods, and the points of intersection by pinpointed universal pivots The rigidity of the rods, that is the inextensibility and inflexibility, and the pinpointing of the universal pivots provide the required Lagrange forces of restraint along and across the lines of zero elongation in the pattern, by offering no resistance to the allowed changes in the orientations of the lines, but linking the mass-points unyieldingly to one another along each line, and at a point of intersection from line to line, such as to offer infinitely strong resistance against the forbidden changes in the length and form of the lines, and in the points of intersection between the lines. The mechanism which is a pinpointed framework of the type of a three dimensional collapsible trellis—has the correct number of allowed degrees of freedom, namely twelve for each region of homogeneous strain, and provides along these degrees an exact model for the changes from an initial to a terminal position of a continuum of mass-ponts which is restrained only by the law of preservation of continuity (see Figs. 1-4 where the mechanism is illustrated for the two-dimensional case) As the strain changes from one homogeneous region to another the law of preservation of continuity introduces for such changes additional restrictions* which can also be incorporated in the trellis model as discussed in chapter B (2) with reference to two-dimensional complex boundary conditions (see Figs 5 to 7) According to the classical theory the continuum of mass-points is subjected to further restraints, according to the law of a dynamical equilibrium of forces, and to the law expressed by an equation of state To satisfy these additional laws the framework of the trellis can be equipped with further Lagrange forces of restraint in the form of appropriate dispositions of masses, and elastic and frictional resistances (springs and dashpots say), and thus made into a mechanical device which can serve as a model of an ideal medium subjected to the classical laws of mechanics

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* A continuous and regular function will here be understood as a continuous function which is univalued, has a univalued inverse, and has continuous derivatives at least up to the second order

† See for instance, W J Ibbetson, "Mathematical Theory of Elasticity," pp 23 and 31. G I Taylor was the first to use the cone of zero elongation in an analysis of three-dimensional strains produced in the plastic flow of single crystals

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* These restrictions—usually referred to as the *conditions of compatibility*—are formulated in the classical textbooks only for infinitesimally small strains

The trellis model discussed above for ideal media may be applied to real materials according to a method specially developed for the purpose When observations are made on a given real material, it is found that the values of the coordinates and forces observed on individual particles of the material deviate to a greater or lesser extent from the theoretical values, that is from the values calculated from the laws of mechanics assumed in an ideal medium. Proceeding, then, from the values observed on individual particles to mean values, associated with appropriately chosen regions in the material, it is found that the deviations between these mean values and the theoretical values can be made as small as desired In this way an ideal medium can be fitted as closely as may be to any given material The method of fitting may be explained with respect to some practical examples Consider first plane sheets of materials in which the structural elements form a loosely interconnected aggregate, as for instance in a flat sliver of cotton Under the action of a pull any pattern of lines or curves drawn on the sliver in the initial position will disintegrate into a pattern of irregular bands in the terminal position, and this makes it necessary to choose, for the formation of mean values, regions with linear dimensions very large compared with those of the structural elements and those of the displacements caused by the pull The fit here will be only a statistical one as there is a considerable difference between the behaviour of individual particles and the mean behaviour of the chosen regions that corresponds to the behaviour of the ideal medium Consider, on the other hand, plane sheets of materials in which a firmly interconnected and apparently continuous aggregate is formed, as in sheets of rubber, Cellophane, polyvinyl chloride etc Here any pattern of lines or curves drawn on the sheet in the initial position, will change under the action of a simple pull, to a pattern in the terminal position in such a way that apparently, i e from a macroscopic point of view, every straight line remains a straight line, every curve of second degree remains a curve of second degree and so on, and every pair of intersecting lines and curves retain their point of intersection intact Accordingly, it is possible here to choose the regions for the formation of mean values so small that from a macroscopic point of view the formation of mean values can be omitted The fit of the ideal medium to the real material approaches here perfection, any individually marked particle in the real material corresponding directly to an individual mass-point in the ideal medium Finally, consider plane sheets of materials of the type of woven or knitted fabrics When one observes here under the action of simple pulls the changes in patterns of markings one finds that the regions required for the formation of mean values are small and correspond to the cells of the periodic repeat of the structure A more detailed investigation reveals the experimental facts that the structure of the fabrics is uniformly periodic before and after the application of a simple pull, and that the threads do not slip over one another where they cross Hence, from a macroscopic point of view it is possible to fit to every woven or knitted fabric an ideal medium directly, i e without the need of formation of mean values, if the fabric is represented by two intersecting series of parallel straight lines drawn in the plane of the fabric along the yarn directions The points of intersection of these lines are referred to as the nodal points

There are many advantages in using the theory of the trellis model as a supplement to the classical theory, as will be seen from the considerations given below.

First, the trellis model, by virtue of its two prominent characteristics, the pinpointing and the existence of lines of zero elongation, draws attention to certain structural features of the materials, visible or sub-microscopic. For materials which have a visible structure, such as woven and knitted textiles attention has been drawn to the pinpointing of the threads at their nodal points persisting over a wide range of stress and strain, and to the strong binding between these points by the threads, which often brings the directions of the threads near to those of the lines of zero elongation These features possess considerable practical and theoretical interest. The pinpointing of the threads not only makes for an even distribution of stress and strain over wide areas, and so increases the resistance of the fabric to external forces, but it also prevents the threads from a destructive rubbing against each other. The existence, in addition, of lines of zero elongation (approximately along the threads) allows of the choice of the best directions for stitched or taped seams and of the alignment of the material to give maximum rigidity in prescribed directions For materials which have a submicroscopic structure, such as crystals, these features are also of interest For elastic deformations, for instance involving only infinitesimally small strains, we may in fact regard the textile fabrics as two-dimensional models of crystals, the nodal points representing the molecules or ions, the threads the strongest bonds which link the molecules or ions to one another The directions of the strongest intermolecular or inter-ionic bonds will then be found to approximate to those of the lines of zero elongation within a wide range of stresses and strains *

Secondly, the trellis model can actually be constructed (from Meccano, say) and then employed as a simple mechanical device whereby one can deduce and predict, without calculation, the performance of materials under various mechanical actions, such as imposed stresses and strains, and boundary conditions Such an application of the model is particularly useful, as some phenomena of great generality can even be predicted from the mere geometry of the framework of the model, irrespective of the masses and elastic and frictional forces involved Consider, for instance, the behaviour of textile fabrics and other materials in the form of plain sheets The corresponding trellis model will have a plane two-dimensional framework of parallelogrammatic cells, constructed by taking two intersecting series of parallel rigid rods and connecting them at their crossing points by pinpointed pivots, round which the two series of rods can rotate relative to one another The model may be made from Meccano strips and may be completed by adding to the framework any arbitrarily chosen disposition of masses, and of elastic and/or frictional resistances Let this model first be laid out in some initial position where it is in its natural state, that is at rest and free from externally applied forces Now let a mechanical action be applied to the model, and observe the ensuing displacement of the model from its initial position to its terminal one, reached at the end of some arbitrarily chosen interval of time In every position during the displacement, the framework of the model or, more precisely, the two intersecting series of rods, will divide the full circle of directions in the plane of the model into four complementary sectors with a pair of mutually perpendicular bisectrices forming the axis of the model It can readily be seen that under any mechanical action whatever a strain will be produced in which the changes in length are so distributed over the full circle of directions that extreme changes occur always along the other two bisectrices, the change along one being a maximum elongation, and that along the other a maximum contraction Consider now a special case in which the model is subjected in its natural state to the application of a simple pull (see Figs 4a to 4d) and compare the results obtained on the model with those obtained on a continuous sheet of material. It follows from considerations of symmetry that if the material in its natural state were isotropic the framework of the trellis model must be so orientated as to have in the initial position one bisector in the direction of the pull and the other at right angles to it

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* For the plastic deformation of crystals, strains of finite amounts may occur, and for these the analogy between textile fabrics and crystals is no longer valid The trellis model may still be used but it must be constructed separately for each pair of initial and terminal positions

The experiment on the model then predicts the characteristic features of the well-known Poisson effect, which are found in experiments made on isotropic sheets of material, such as sheets of rubber, Cellophane, polyvinyl chloride, etc , with an extreme elongation occurring along the direction of the pull, and an extreme contraction at right angles to it If, on the other hand, the material in its natural state were anisotropic, the orientation of the framework of the trellis to the direction of the pull would vary with the direction of the pull in the material For an arbitrarily chosen direction of pull, the framework in the initial position will be so orientated that the direction of the pull is in general inclined at a finite angle to both bisectrices. The experiments made on the model will here predict a modified Poisson effect with maximum elongations and contractions occurring not parallel and perpendicular to the direction of the pull but along the bisectrices, and in addition there will be a rotation of the directions of maximum elongation and contraction, which brings, in the terminal position, the direction of maximum elongation nearer to that of the pull This motion gives the impression that the material is taking an "*evading action*", by rotating round and having its maximum extension in a direction different from that of the pull Experiments were made on anisotropic sheets of materials, such as sheets of leather and of woven and knitted textile fabrics, and these experiments have confirmed, in a rather striking manner, the various predictions based on the trellis model, such as the modified Poisson effect and evading action Still more impressive is the use of the trellis model under mechanical actions with complex boundary conditions For such actions and conditions it is possible to obtain for materials in the form of plane sheets, and in particular for woven fabrics, a first-order approximation to the strain distribution in the sheet by performing a model experiment on a suitably constructed trellis (see Figs. 1—8)

Finally, the trellis model leads to the development of new types of stretching device which allow the imposition, on a plane sheet of material, of homogeneous states of strains and/or stresses, arbitrarily selected within certain limits, as are required in the testing of materials, as well as in many industrial processes

The commonly available stretching devices are rarely suited to this purpose, as they generally induce a heterogeneity of stresses and strains such as is shown in tensile testing by the waisting and/or buckling, of the specimen Suppose, for instance, the problem is to impose on a rectangular sheet of material a homogeneous state of strain, defined by a given lengthwise extension and a given widthwise contraction In the ordinarily available stretching frames the sheet would be gripped along the edges of the rectangle, and here the intended state of strain could not be produced homogeneously by a movement of the grips, since the portions of the sheet in the vicinity of the edges are restrained from extending or contracting by the rigidity of the grips while the more distant parts of the sheet are almost free from restraint By contrast, the theory of the trellis model allows us to impose homogeneously the intended strain by gripping the specimen in the initial position along the lines of zero elongation, predetermined for this position by the intended strain, and moving these grips in a "lazy-tongs" motion which conforms to the change in orientation of the lines of zero elongation from the initial to the terminal position The grips can conveniently be linked by pinpointed joints in a parallelogram framework which would perform the required "lazy-tongs" motion and thus constitute a suitable stretching device If it were desired to impose homogeneously a given state of stress, a similarly constructed stretching device could be used, but the procedure would be somewhat more complicated It would here be necessary to determine, by preliminary experiments on the material, the corresponding state of strain for the given state of stress, and then impose the strain by means of the stretching device in the manner described above Where the intended stress is a simple pull lengthwise of the rectangular specimen of the material, simplified forms of the stretching device may be used

A. THEORY OF THE TRELLIS MODEL

In the Mechanics of Continuous Media, the classical procedure deals first, in the Theory of Strain, with the Kinematics, then, in the Theory of Stress, with the Dynamical Equilibrium, and finally, in the Theory of the Mechanical Properties of the Media, with the Relationship between the Stresses and Strains Each of these theories is based on certain assumptions, the theory of strain on the assumption that the postulate of preservation of continuity is valid, the theory of stress on the assumption that Newton's laws of inertia apply, and the theory of the mechanical properties of the media on the assumption of the existence of some relationship between the strains and stresses and their partial derivatives in space and time All these assumptions together determine completely the behaviour of the medium under any given mechanical action, and we may in fact derive from them an explicit description of the behaviour by formulating the assumptions as differential equations, and integrating these over space and time for the boundary conditions imposed on the medium by the given mechanical action. We shall follow the classical procedure in our exposition of the theory of the trellis model In the first section, dealing with the *theory* of strain, we construct a mechanical model—the trellis model—the kinematics of which conform to that of a medium for which the postulate of preservation of continuity holds good In the second section, dealing with the *theory of stress,* the trellis model is fitted out with a mass distribution such that the Dynamical Equilibrium of the model conforms to that of a medium for which Newton's laws of inertia are valid Finally, in the third section, dealing with the *theory of the relationship between the stresses and strains,* the trellis model is adapted to the mechanical properties of the medium by equipping the model with appropriately chosen elastic and/or frictional forces of restraint, represented, say, by springs and dashpots

(1) Theory of Strain

The classical theory associates with every displacement from an initial to a terminal position some *state of strain,* and we shall use here the word strain in a generalised sense to indicate any displacement of the medium from one position to another, irrespective of whether or not changes in length are involved The postulate of the maintenance of continuity will restrict the possible displacements, and consequently the possible states of strain, by requiring that, for every mass-point the vector of the displacement and its space derivatives (at least up to the second order) should be continuous functions of the space coordinates of the mass-points of the continuum The state of strain compatible with the postulate will, in general, vary from mass-point to mass-point, and will be specified separately at each point by the *local strain* at that point

If in some region the displacement vector is a linear function of the space coordinates, the state of strain is said to be *homogeneous* throughout that region In general the function may not be linear and the state of strain will then be termed *heterogeneous*

Owing to the maintenance of continuity, the displacement vector can be developed in the infinitesimal neighbourhood of each mass-point into a power series of the coordinate differentials and, neglecting terms of second and higher degree against the linear terms, we shall regard the displacement vector as a linear function of the coordinates, and accordingly specify by this linear function the local strain at the mass-point. Thus the local strain will always be a homogeneous one within an infinitesimal region

We can deduce from the postulate of the maintenance of continuity various mechanical models The most general such model is found as follows. In the initial position we choose arbitrarily three mutually intersecting families of curves and consider what happens to them in a displacement of the medium from the initial to a terminal position. It follows from the maintenance of continuity that throughout the displacement all points of intersection are maintained as if the families of curves were *pinpointed* to one another at all points of intersection, *while at the same time changes in orientation, length and form may occur in the elements of the curves which lie between two consecutive points of intersection The general model so deduced consists of a scaffolding of three mutually intersecting families of curvilinear threads which are pinpointed to one another at their points of intersection, and which are so pliable and extensible that the elements of the threads between two consecutive pinpoints change their orientation, form, and length in accordance with the requirements of the state of strain produced by the displacement from the initial to the terminal position This scaffolding model may conveniently be used for problems more general than those dealt with here.

In the present paper we shall restrict ourselves to a more special model, termed the *trellis model,* which we obtain as follows We deduce from the postulate of maintenance of continuity that the medium suffers at every mass-point a local strain, which corresponds to a vector of displacement that changes only linearly in the neighbourhood of the mass-point, provided the neigbourhood is chosen sufficiently small to neglect terms of second degree against linear terms.

Hence, passing from an initial to a terminal position, all infinitesimal curves and surfaces will preserve their degree as an invariant, so that infinitesimal straight lines and planes will remain straight lines and planes while infinitesimal curves and surfaces of second degree will remain of second degree, etc In particular we find that there will be at every mass-point, fixed in the medium, two infinitesimal surfaces of second degree, termed the local *strain ellipsoid* and the local *reciprocal strain ellipsoid,* which are both centred on the mass-point and change their form, respectively, from a sphere in the initial position to an ellipsoid in the terminal position, and conversely from an ellipsoid in the initial position to a sphere in the terminal position. The local strain at the mass-point is completely determined by the two complementary aspects which are provided by the forms of the local strain ellipsoid and reciprocal strain ellipsoid in the initial and terminal position.

In each position, the strain ellipsoid and the reciprocal strain ellipsoid define by their common centre and their line of intersection, a conical surface, fixed in the medium, and termed the *cone of zero elongation,* along the generating lines of which the infinitesimal elements radiating from the central mass-point suffer zero changes in length between the initial and terminal position There are thus in each position, centred on the same mass-point, three surfaces of second degree, the reciprocal strain ellipsoid, the strain ellipsoid and the cone of zero elongation These three surfaces have in common one triple of mutually perpendicular axes, fixed in the medium and aligned along directions in which the infinitesimal elements radiating from the centre suffer extreme changes in length We define for the local strain in either position three *main axes* which coincide in directions with the common axes of the three surfaces, and which have numerical values, termed *main values,* identical with the ratios of the terminal length to the initial length taken along the directions of the main axes

Based on the above conceptions we can now elaborate the general scaffolding model We choose the three families of curves sufficiently close so that the infinitesimal parts between any two consecutive pinpoints can be approximated to by infinitesimal straight lines, in addition we provide that at every pinpoint the three curves passing through it have tangents which lie along the cone of zero elongation at the pinpoint The model so constructed is termed a *trellis**, since in every element of volume it can expand and contract only trellis-like by changing the relative orientations of its infinitesimal members between consecutive pinpoints while maintaining unchanged from the initial to the terminal position the points of intersection and the length and form of each infinitesimal member At every pinpoint we shall attribute to the trellis *three main axes*, which, by definition, are identical with those of the cone of zero elongation, and thus are co-axial with those of the local strain at that point The infinitesimal members of the trellis between two consecutive pinpoints behave as if they were *rigid rods*, unbendable and inextensible The spacings between the trellis lines do not affect the movement of the model so that we are at liberty to choose arbitrarily in each family any density, or density distribution of trellis lines For simplicity, we shall choose the density constant of the same value in all the families so that the trellis is made up of infinitesimal cells each of which approximates to a rhombohedron

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* Consider, in the initial position, various series of mass-points infinitely near to one another and aligned respectively along individual curves or surfaces in the neighbourhood of a point of intersection Throughout the displacement from the initial to the terminal position the point of intersection will be preserved intact, since a gliding over one another of the intersecting curves or surfaces would destroy the continuity, by separating in the terminal position, by finite amounts, the series of mass-points aligned along one curve or surface, from the series aligned on another

Considerable simplifications arise in the two-dimensional case which is illustrated in Figs 1 and 2 Here the displacements of the mass-points are limited to those that are parallel to one plane and we restrict ourselves to the investigation of that plane In the general case of a heterogeneous state of strain we have to consider separately for each individual mass-point in the plane its infinitesimal neighbourhood, and define there the intersections with the plane of the three local surfaces of second degree and their common axes respectively as three local curves of second degree, termed the *strain ellipse*, the *reciprocal strain ellipse*, the *pair of lines of zero elongation*, and their common axes In the special case of a homogeneous state of strain, the consideration for any one mass-point is exactly the same as above, only here the same local surfaces and axes will apply for every mass-point in the region of homogeneity Figs 1a and 1b refer, respectively, to the initial and terminal positions and show the local strain at a mass-point The intersections with the plane of the three local surfaces, and their common axes appear here as curves of second degree, and their axes Proceeding from the initial to the terminal position the local strain ellipse (marked in dotted lines) and the local reciprocal strain ellipse (marked in chain lines) are shown to change their form respectively from a circle to an ellipse, and conversely from an ellipse to a circle The local pair of lines of zero elongation (marked in thick full lines) which join in either position crosswise through the central mass-point, the four points of intersection between the strain ellipse and the reciprocal strain ellipse change from one position to another as if they were rigid rods pinpointed to one another at the centre where they cross, each such rod suffering only a change on orientation but retaining rigidly its length and form The main axes (marked in thin full lines) form in either position a part of mutually perpendicular lines which bisect the two complementary angles between the two lines of zero elongation We distinguish the axes of the local strain as the *major and minor axis* and identify them as the bisectors of the angles which respectively decrease and increase between the initial and terminal positions, the major (minor) axis of the local strain is thus identical with the major (minor) axis of the strain ellipse and with the minor (major) axis of the reciprocal strain ellipse.

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* The trellis model will be a real mechanical model when the cone of zero elongation is real (see preceding footnote) and in this paper all applications will be confined to this case When the cone of zero elongation is complex, the trellis model becomes complex too and then its construction in real space is not possible However, replacing again the geometrical construction by an algebraic procedure, we can use the model as a scheme of calculation irrespective of whether it be real or complex If in such complex cases a mechanical model is required in real space, we can fall back either on the general scaffolding model or on an appropriate superposition of three trellis models working simultaneously

In the general case of a heterogeneous state of strain we find a plane trellis consisting of two mutually intersecting families of curves which are pinpointed where they cross and which are so drawn that their infinitesimal elements between two consecutive pinpoints are straight and coincide at each mass-point respectively with the two lines of zero elongation In the special case of a homogeneous state of strain, the plane trellis will be a linear one, and such a *plane linear trellis* will be an exact replica of the ordinary type of garden trellis consisting of two mutually pinpointed families of parallel rigid rods Taking any one cell again as a representative for the whole trellis we find a model consisting of a pinpointed parallelogrammatic frame of four

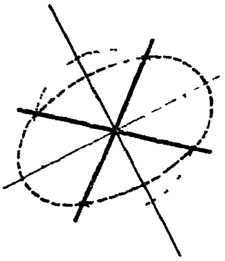

Fig 1 (*a*)

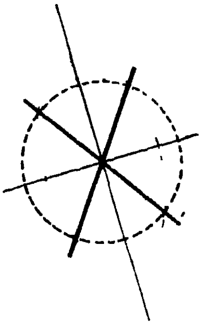

Fig 1 (*b*)

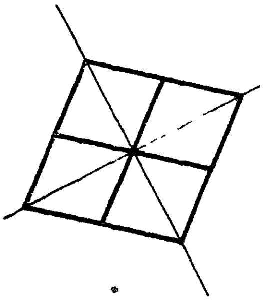

Fig 2 (*a*)

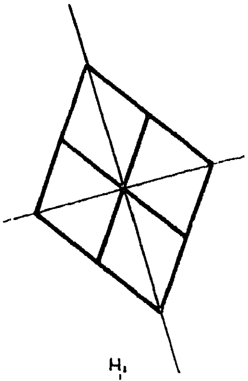

Fig 2 (*b*)

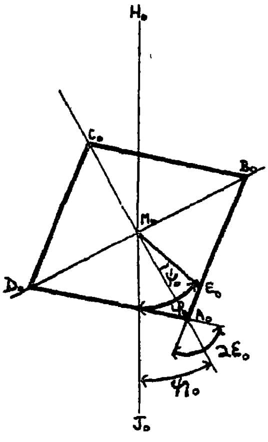

Fig 3 (*a*)

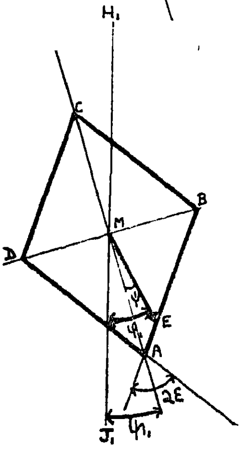

Fig 3 (*b*)

rigid rods. The maximum elongation and contraction of such a trellis occur in the two mutually perpendicular directions which bisect the two supplementary angles formed by the trellis lines at each pinpoint—these two directions in the initial and terminal states being the major and minor axes of the strain If the trellis is constructed from sets of equidistant parallel lines, thus forming rhomboidal " cells ", the principal axes are the diagonals of these rhombuses.

The local strain shown in Fig 1 is represented by a trellis model shown in Fig 2

Four rhombohedral cells of the trellis, surrounding the central mass-point, are shown respectively in Fig 2 under (*a*) and (*b*) in the initial and terminal positions. They are constructed from the corresponding Figs 1a and 1b by making the lines of the rhombohedral cells of equal length and parallel to the lines of zero elongation The main axes of the trellis are shown by those diagonals of the rhombohedral cells which pass through the central mass-point; these diagonals are of course parallel to the main axes of the curves of second degree shown in Fig 1

For all states of strain there is a perfect equivalence between the performance of the trellis model and the production of the state of strain according to classical theory In both the classical and the trellis theory, we decompose the local strain, or the homogeneous strain in some finite region, into a succession of those simple geometrical operations, termed *translation, rotation* and *deformation* The operations are so defined that the classical medium, including the trellis model, passes locally, or within the region of homogeneous strain, into the terminal position by applying these operations in ordered succession to the initial position We find that the translation equals the displacement vector of the central mass-point and as a geometrical operation transports the medium and the model along it rigidly and parallel to itself The rotation turns the medium and the model rigidly round an axis through the central mass-point about an angle such as corresponds to the change in orientation of the main axes of the strain from their directions occupied in the initial position along the axes of the reciprocal strain ellipsoid to those occupied in the terminal position along the axes of the strain ellipsoid Finally the deformation stretches the medium and the model in a triad of mutually perpendicular directions along the main axes of the strain to extents that are proportional to the main values of these axes The order of succession in which the three simple geometrical operations are applied matters only in so far as the deformation has to be carried out along the directions of the main axes in the initial or terminal position according to whether the deformation precedes or follows the rotation It may happen that in a special state of strain one (or more) of the three simple geometrical operations is (are) zero, and we shall speak in particular of an irrotational, or pure strain when the rotation of the main axes is zero

We can describe in a quantitative way the relationship between the classical strain and its trellis model by considering what happens to a vector drawn from the central mass-point as origin in an arbitrarily chosen direction (for heterogeneous states of strain the vector must be infinitely small whilst for homogeneous states of strain it may be of finite length within the region of homogeneity) The vector changes from the initial to the terminal position with regard to its point of origin, its direction, and its length Both in the classical and in the trellis theory we describe these changes in terms of vector components taken along directions fixed in the material In the classical theory these directions are chosen along the main axes of the strain and here the initial and terminal components differ from one another in their points of origin, in their directions, and in their length In the trellis theory the directions are chosen along the lines of zero elongation, and here the initial and terminal components differ in their point of origin and in their directions, but not in length. Equating the resultant changes in the vector from two sets of components we gain the required quantitative relation between the classical strain and the model

We can now develop the geometry of strain according to a plane linear trellis by considering a single rhombohedral cell in the initial and final position In Fig 3 we show the initial and terminal positions, respectively, under (*a*) and (*b*) and adopt a notation such that identical elements in the medium bear the same symbol in the two positions respectively with and without a subscript zero We have indicated such elements in the two positions according to the scheme given below In order to specify the orientation of the medium to a fixed direction in space, we have drawn in Figs 3a and 3b two parallel lines as lines of reference through the central mass-point These two lines of reference and the angles referring, respectively, to them in the initial and terminal position are corresponding elements which, however, need not be identical in the material (i e. need not be made up of the same mass-points) For these elements we adopt a notation in which they bear the same symbol in the two positions, respectively, with a subscript zero and one Finally, we adopt the convention that angles deviating clockwise from the line of reference will be counted positive while those deviating anti-clockwise will be counted negative

The trellis model will be fully specified for the central mass-point (M_0 and M) by giving in the two positions respectively the opening angle ($2\epsilon_0$ and 2ϵ) and the angle (χ_0 and χ_1) between the major axis of the strain and the line of reference fixed in space This angle characterises the orientation in space of the model Decomposing the strain into a succession of translations, rotations and deformations we can specify the translation by a vector v, say, where

$$v=M_0M \tag{1}$$

the rotation corresponding to the change in direction of the main axes by an angle ω, say, where

$$\omega=\chi_1-\chi_0 \quad . \tag{2}$$

and the deformation corresponding to a change in length along the main axes by the ratios, *a and b, say, where

$$a=\frac{\cos\varepsilon}{\cos\varepsilon_0} \tag{3}$$

$$\text{and } b=\frac{\sin\varepsilon}{\sin\varepsilon_0} \tag{4}$$

which gives for the opening angle of the trellis the equations

$$\tan^2\varepsilon_0=\frac{a^2-1}{1-b^2} \tag{5}$$

$$\text{and } \tan^2\varepsilon=\frac{b^2(a^2-1)}{a^2(1-b^2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{6}$$

Similarly, we may specify the arbitrary vector in the two positions by giving its length (r_0 and r) from the origin in the central mass-point (M_0 and M), and the angle (φ_0 and φ) with the line of reference fixed in space According to the classical theory the vector is resolved into components taken along the main axes of the strain, and here each such component suffers a translation, rotation and deformation as defined above. According to the trellis theory, on the other hand, the vector is resolved into components along the lines of zero elongation and each such component remains invariant in length and suffers only a translation and rotation By compounding in either theory the changes of the component we obtain the change in the vector itself. We then find that the vector suffers a translation u, say, equal to v, according to

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* We deduce by comparison of Figs 3a and 3b that $a=\frac{MA}{M_0A_0}$ Considering then the triangles AMB and $A_0M_0B_0$ we have $MA=AB\cos\varepsilon$ and $M_0A_0=A_0B_0\cos\varepsilon_0$ with $AB=A_0B_0$ since the sides of the rhombus are lines of zero elongation Continuing these results we find $a=\frac{\cos\varepsilon}{\cos\varepsilon_0}$ and proceeding similarly we deduce $b=\frac{\sin\varepsilon}{\sin\varepsilon_0}$.

$$u=v=M_0M \qquad \text{(7)}$$

together with a rotation given by the angle $(\varphi_1-\varphi_0)$ which is the sum of the angle, ω, of rotation of the main axes, and the angle $(\psi-\psi_0)$ of rotation resulting from the disproportional changes of the components of the vector viz :—

$$\varphi_1-\varphi_0=\omega+(\psi-\psi_0) \qquad \text{(8)}$$

where

$$^{*}\ \tan\psi=\frac{\tan\psi_0\ \tan\varepsilon}{\tan\varepsilon_0} \qquad \text{(9)}$$

and finally a deformation with a change in length, λ say, defined as the ratio r/r_0 which is made up of the changes of the components of the vector along the main axes, viz —

$$\lambda=r/r_0=\sqrt{\left(\frac{\cos\varepsilon}{\cos\varepsilon_0}\cdot\cos\psi\right)^2+\left(\frac{\sin\varepsilon}{\sin\varepsilon_0}\times\sin\psi\right)^2} \qquad \text{(10)}$$

which, in consideration of (9) can also be written as

$$\lambda=\frac{\sin\varepsilon}{\sin\varepsilon_0}\cdot\frac{\sin\psi_0}{\sin\psi} \qquad \text{(11)}$$

The above discussion refers only to the state of strain set up in a medium by a displacement from an initial to a final position We must now consider as well the state of stress

(2) Theory of Stress

In each position of the medium, and irrespective of the strain or motion present, the classical theory defines a certain *state of stress* by the traction forces per unit area at every mass-point, and assumes that for every portion of the medium a dynamical equilibrium is established in which the state of stress, the body forces, and the forces of inertia participate as required by Newton's laws of inertia The state of stress so defined will, in general, be heterogeneous, that is varying in the medium from mass-point to mass-point, and may be specified at each mass-point by the *local stress* at that point, in a special case the state of stress may be *homogeneous* in some region and then the local stresses will be the same for all mass-points in that region Neglecting again in the infinitesimal neighbourhood of a mass-point infinitesimal terms of second and higher order against terms of first order we can regard the local stress as a homogeneous one in some infinitesimal region If we imagine the medium to be divided into two portions by a plane passing through a given mass-point, we find the local stress, that is the traction force

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[*] We deduce from the triangles $E_0M_0A_0$ and $E_0M_0B_0$ according to the sine law

$$\frac{A_0E_0}{B_0M_0}=\frac{\sin\psi_0}{\sin\varepsilon_0}$$

and

$$\frac{B_0E_0}{E_0M_0}=\frac{\sin(90^\circ-\psi_0)}{\sin(90^\circ-\varepsilon_0)}=\frac{\cos\psi_0}{\cos\varepsilon_0}$$

By dividing the first equation by the second we find

$$\frac{A_0E_0}{B_0E_0}=\frac{\tan\psi_0}{\tan\varepsilon_0}$$

Similarly we find from the triangles EMA and EMB $\frac{AE}{BE}=\frac{\tan\psi}{\tan\varepsilon}$

Considering, then, that the distances along the lines of zero elongation do not change by passing from the initial to the terminal position we find

$$A_0E_0=AE$$

$$B_0E_0=BE \text{ and hence } \frac{\tan\psi}{\tan\varepsilon}=\frac{\tan\psi_0}{\tan\varepsilon_0}$$

Multiplying this equation by $\tan\varepsilon$ we obtain equation (9) per unit area which is required to hold the two portions of the medium together, to possess, in general, a normal and a shearing component with respect to the dividing plane, letting, then, the dividing plane take up all orientations in a solid angle round the mass-point in consideration, we deduce, on applying Newton's laws of inertia to all the portions of the medium and neglecting terms of second and higher order, that the local stress can always be represented by a surface of second degree Accordingly, at each mass-point there will be three mutually perpendicular planes to which the local stress is entirely normal and over which all shearing components are zero The normals to these planes are called the *directions of the main axes of the local stress,* and the numerical values of the stresses in these directions are termed the *main values of a stress.* In general all three main values differ from zero and the state of stress extends accordingly in all three dimensions of space In special cases, however, of which we shall make a detailed study, one or two of the main values are zero

Particularly simple states of stresses arise when the local stresses are the same throughout some finite region. The state of stress is then termed homogeneous in that region, and has throughout it the same directions of main axes and the same main values. A state of stress which is homogeneous in some region and has only in one direction of space a main value different from zero is termed a *simple pull* in that direction.

The trellis model can easily be adapted so as to comply with the assumption of a dynamical equilibrium as postulated in the classical theory of stress in accordance with Newton's laws of inertia All we have to do is first to define the trellis lines according to the strain (as indicated in the preceding section) and then to concentrate the whole mass of the medium along these lines.

(3) Theory of the Relationship between Strains and Stresses

Let a medium be considered first in the natural state, i.e , at rest and free from externally applied forces Subjecting the medium then to some mechanical action we find that the natural state will change into a strained and stressed state which will vary with any change of the particular action applied We can determine in the medium, for every applied mechanical action, the strains and stresses which coexist at every instant of time and at every point in space, and the space and time derivatives of such strains and stresses The classical theory assumes that for a given medium there is a relationship between the coexisting strains and stresses and their derivatives in space and time, and that this relationship is the same for all states of the medium (natural or strained and stressed), independent of the mechanical action applied, and independent of the particular instant of time and the point in space under consideration. The relationship is thus characteristic for the medium under examination, and the mechanical properties of the medium such as elasticity, viscosity etc can be defined and specified by the constants in this relationship Combining the relationship with the two principles of maintenance of continuity, and of dynamical equilibrium, discussed in the two preceding sections, we obtain for an infinitesimally small portion of the medium a characteristic equation of motion in the form of a set of partial differential equations, and deduce from it the behaviour of any finite portion of the medium under any mechanical action by integrating the equation of motion over space and time for the particular boundary conditions imposed by the action We can distinguish between media of different kinds, each kind being characterised by one equation of motion, and accordingly by one set of values of the parameters which specify the mechanical properties of the medium

We shall group the different kinds of media into classes, according to the symmetry, or lack of symmetry, in space and time which the media possess in their natural state, i e according to the invariance or variability of the equation of motion of the media against transformations of the coordinates of space and time. The reason for such a classification is that the media will exhibit under mechanical actions certain phenomena with characteristics that can be predicted already from the symmetry class to which the medium belongs

With regard to the time coordinates it suffices here to distinguish between two symmetry classes, a general one, termed ***unstable,*** which embodies all media for which there is an appreciable variation with the time coordinate on the equation of motion, and a special one termed ***stable,*** for which no such variation can be detected. The media so classified as unstable, will change their mechanical properties in time even when they are at rest and free from mechanical actions, while the media classified as stable will, under these conditions, retain their mechanical properties invariant With regard to the space coordinates we must fix in space, once and for all, a system of reference for such coordinates, and examine the results of changes in the coordinates separately for those due to parallel displacements of the system, and those due to a change of orientation.

The terms ***heterogeneous*** and ***homogeneous*** will be used to denote symmetry classes of media which are characterised respectively by a variability or invariance under parallel displacements, and it will be convenient to subdivide the homogeneous classes into ***continually homogeneous*** and ***periodically homogeneous*** ones according to whether the invariance under parallel displacements covers a continuous range of displacements or a periodic set of discrete displacements Similarly we shall use the terms ***anisotropic*** and ***isotropic*** to denote symmetry classes of media which are characterised, respectively, by a variability or invariance under changes of orientation If and when necessary, a further subdivision of all the above mentioned symmetry classes can be introduced

It is of interest to visualise clearly how the ideal medium of the classical theory is represented by the trellis model This medium differs from a hypothetical three-dimensional continuum of free mass-points by the restraints which are imposed on it through the equations between the coordinates of the points, the equations make the medium conform to the various assumptions of the classical theory According to Lagrange, we can interpret every such equation as a restraint to the free mobility, and replace the equation by the introduction of appropriate forces of restraint There will be three sets of forces of restraint in the ideal medium, corresponding respectively to the three assumptions of the classical theory, and the trellis model represents these sets of forces by appropriate mechanical devices Considering a differential cell in the hypothetical continuum, of free mass-points, we find in it an infinite number, N say, of mass-points, each with three degrees of freedom, so that there are altogether an infinite number, $3N$, of degrees of freedom per cell Now the assumption of the preservation of continuity allows, for the mass-points in the cell, only 12 degrees of freedom, and forbids all the other $3N$-12, since in the infinitesimal cell the displacement vector must vary linearly with the coordinates of the mass-points[*] Now the reduction in the number of degrees of freedom from $3N$ to twelve can be interpreted according to Lagrange as a restraint by infinitely large forces along the forbidden degrees of freedom, and in the trellis model these forces of restraint are represented by the rigidity of the framework of the model, that is, by the inextensibility of the trellis lines and their pinpointing to one another at the points of intersection The two remaining assumptions of the classical theory do not reduce the number of degrees of freedom any further, but impose on the allowed twelve degrees of freedom finite forces of restraint The assumption of the existence of a dynamical equilibrium corresponds to the imposition of forces of inertia, and these are represented in the trellis model by an appropriate distribution of masses along the framework of the model Finally, the assumption of a relationship between the strains and stresses corresponds to the imposition of elastic and/or frictional forces, and these are represented in the model by springs and dashpots appropriately connected to the constituent members of the model Thus, it is possible to construct a trellis model which reproduces the behaviour of a medium of any kind, for given mechanical actions imposed on it, by choosing a pinpointed framework of rigid trellis lines in accordance with the imposed strain, fixing masses to this framework in accordance with the laws of the dynamical equilibrium, and finally regulating the relative movements of the trellis lines by elastic and frictional restraints, such as springs and dashpots The above construction of a trellis model completes in principle the theory of this model We shall not discuss the details of the construction in this paper but leave it to a separate investigation*.

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[*] The twelve degrees of freedom for a differential cell are formally deduced by expressing the three components of the displacement vector, u_i say, as a general linear function of the co-ordinates, x_k say, viz , $u_i = a_i + \Sigma_k b_{ik} x_k$ and associating one degree of freedom with each of the twelve arbitrary constants a_i and b_{ik}

To illustrate the correspondence under simple pull between the behaviour of an anisotropic material and that of the trellis model consider the general case where the direction of pull is arbitrarily chosen with regard to the structure of the material Figs 4 (*a*) and (*b*) refer to the initial and terminal position of a trellis model constructed from four rigid rods that are joined to one another by pinpointed pivots to form a collapsible rhombus The direction of the pull is arbitrarily chosen with respect to the trellis structure, and maintained in space in a vertical direction, marked in Figs. 4 (*a*) and (*b*) by the vertical lines through the centre A strain ellipse has been lined out to indicate the changes in length that occur over the full circle of directions When an experiment on an actual model is performed a strain is obtained which exhibits all the various characteristics of pinpointing, linearity, Poisson effect and evasion action discussed above The correspondence in behaviour of a material is shown in Figs 4 (*c*) and (*d*) which refer to the initial and terminal positions of a specimen of woven fabric The specimen has been cut out along an arbitrarily selected direction in the weave structure, and has then been subjected along this direction to a simple pull There is imprinted on the specimen a pattern showing in the two positions the strain ellipse, the direction of pull (marked as a vertical line in the middle of the specimen) and the weave structure (marked by two lines along a warp and a weft thread, with the warp line bearing an arrowhead for distinction)

B APPLICATIONS OF THE TRELLIS MODEL

We are interested here particularly in the application of the theory to media which are in a stable and homogeneous symmetry class and which, in addition, are solid in the sense that a state of static equilibrium is reached under any state of stress which is maintained stationary in the medium. Every such medium will have a well-defined natural state, i e a state in which it is at rest and free from external forces For convenience we shall standardise the initial position such that in it the medium is in its natural state, all strains to a terminal position being measured from that state

When we apply to such a medium a state of stress which is stationary relative to a system of reference fixed in the medium, we find that in time a *static equilibrium* is reached

Studying, then, the static equilibrium of the said medium, we find from the relationship between the states of stresses and strains together with the

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* Even in the simple case of a two-dimensional sheet of an isotropic medium that obeys Hooke's law we find that the equipping of the trellis model with springs requires a rather elaborate procedure In accordance with the two independent elastic constants in Hooke's law, we need two independent sets of springs, one representing the modulus of compressibility by which the framework of the model is isotropically suspended in a circular rigid ring, and another, representing the shearing modulus by which the two series of trellis lines are restrained from rotating against one another

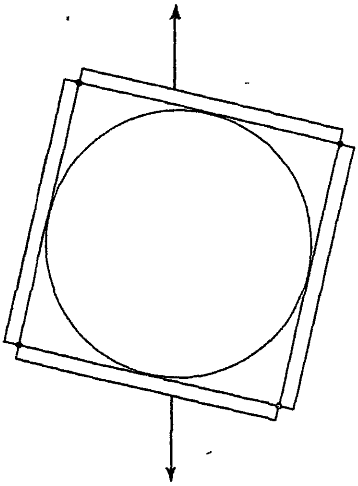

Fig 4 (*a*)

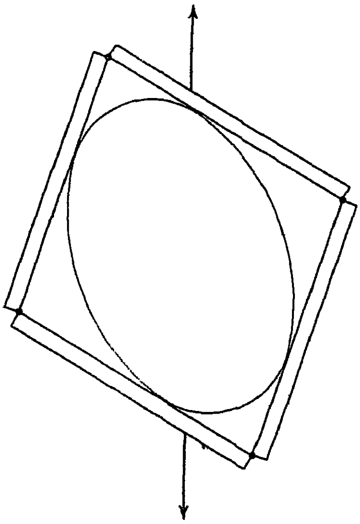

Fig 4 (*b*)

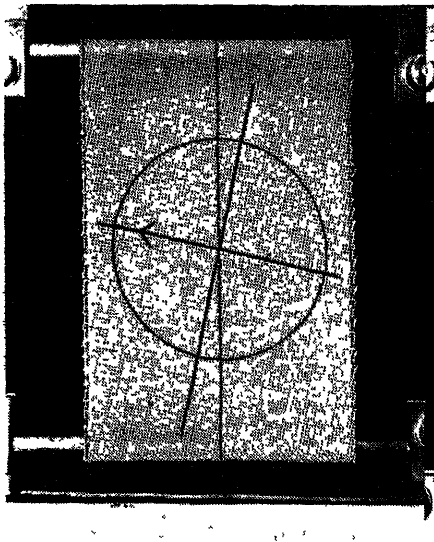

Fig 4 (*c*)

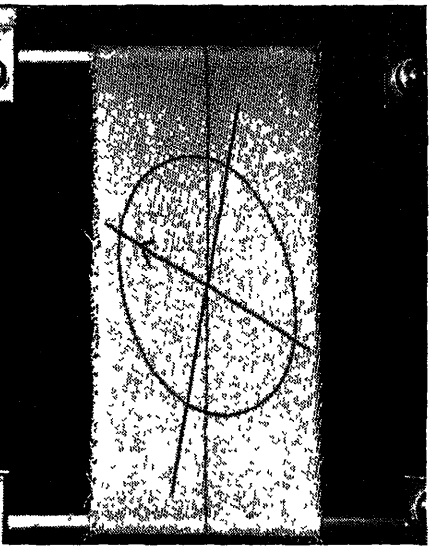

Fig 4 (*d*)

principles of dynamical equilibrium and of continuity, that a state of stress homogeneously applied over some region produces a state of strain which is homogeneous over the same region All the forces of inertia are here zero since they do not operate under static conditions The main axes of stress always indicate the conditions along which the forces which tend to change the length have extreme values, while the main axes of the strain indicate the directions along which the extreme changes in length actually occur In the general case, that is for an anisotropic medium and an arbitrarily chosen triad of main axes of stress, there will be a deviation between the directions of the main axes of stress and those of the strain, so that the medium appears to take an evading action in which the maximum changes in length actually occur in directions which differ from those along which the forces have maximum values. Where the evading action occurs the strain (from the natural state) is compounded of a pure strain and a rotation Only in special cases, that is for isotropic media, or for special directions in anisotropic media, will there be no evading action, that is, there will be a coincidence of the main directions of stress and strain, the strain being in this case a pure strain. These reactions of the medium can be predicted from model experiments carried out on an actual trellis which may conveniently be constructed from the rigid strips and the pinpointed pivots of a "Meccano" set. By way of example we shall discuss some cases of practical importance.

(1) The State of Strain under a Simple Pull

In the special cases in which the simple pull is exercised either in an isotropic medium along an arbitrarily chosen direction, or in an anisotropic medium in some special direction, we find from the classical theory that there is no evasion action and that a static state of equilibrium is reached in which the state of strain is a homogeneous and pure strain with maximum changes in length occurring in the direction of the pull and in all directions at right angles to it *Poisson* was the first to discover this phenomenon experimentally and to show that the changes in length in the direction of the pull are elongations, whilst those in the directions at right angles are contractions In his honour it is customary to use the term *Poisson ratio* to denote the ratio of the relative changes in length in the directions of the pull to that in a direction at right angles to it We note the remarkable effect of a change in length (contraction) occurring in the directions perpendicular to that of the pull along which the main values of the stress are zero

In the general case in which the simple pull is exercised along an arbitrarily chosen direction in an anisotropic medium, we find similarly from the classical theory that there will be an evading action, and that a state of static equilibrium will be reached in which a homogeneous state of strain exists that is compounded of a pure strain and a rotation The pure strain will show a change of length along all its three main axes, according to a more complex Poisson effect, and the rotation will take place according to the change in direction which the three main axes of the strain suffer in transit from the initial to the terminal position The evading action thus shows two characteristics appearing respectively in the pure strain and in the rotation. As regards the pure strain, we find that in the initial and in the terminal positions the direction of the maximum elongation does not coincide with that of the pull, the angle between the two directions being termed the angle of evasion As regards the rotation we find that in passing from the initial to the terminal position the angle of evasion diminishes, the medium thus tending to bring the direction in which the maximum extension occurs nearer to the direction in which the maximum stress is applied

The trellis model accounts in a particularly simple way for the Poisson phenomena and for the evasion action, especially when a two-dimensional case is considered in which we are interested only in a plane parallel to the direction of the pull. For the static equilibrium we have then to consider only a two-dimensional homogeneous state of strain where the trellis model can be represented by a rhombus with diagonals extending parallel to the main axes of the strain If, then, we choose the direction of pull arbitrarily in an isotropic medium, or in an appropriate way, in an anisotropic medium, we have in the initial position the trellis so orientated that its main axes, i e the diagonals of the representative rhombus, extend respectively in directions parallel and perpendicular to that of the pull. Applying then the pull to the model, and fixing it in a terminal position corresponding to the static equilibrium, we find that the representative rhombus, and with it the whole trellis will perform no evading action, but will change from the initial to the terminal position according to a pure strain in which a maximum elongation along the diagonal parallel to the direction of the pull is accompanied by a maximum contraction along the other diagonal, at right angles to the direction of the pull, as required by the Poisson ratio If, on the other hand, we consider the general case, i e , choose an arbitrary direction of pull in an anisotropic medium, we have in the initial position the trellis so orientated that the diagonals of the representative rhombus extend in generally inclined directions to that of the pull Applying here the pull to the model and fixing it again in a terminal position corresponding to the static equilibrium, we find that the representative rhombus, and with it the whole trellis, will perform an evading action In this evading action the state of strain will be compounded of a pure strain and a rotation The pure strain will take place in accordance with the Poisson ratio It will have a maximum elongation and contraction occurring respectively along the two diagonals of the rhombus, and these will here form with the direction of the pull, angles, termed respectively the *angle of evasion* and its complement. In addition, a rotation will take place as the diagonals of the rhombus turn round relative to the direction of the pull which has been maintained fixed in the medium and in space

Under a simple pull, the trellis which operates in the initial position will vary in general with the mechanical properties of the medium, with the direction of the pull, and with the amount of pull applied For many media, however, such as rubber, textile fabrics, etc., it has been found that the variation of the trellis with the amount of pull is, within a certain range of pulls, so small as to be negligible, and for these media the state of strain may be represented by the same trellis over a wide range For other materials, a separate trellis model has to be constructed for each ordered pair of initial and terminal positions In the plastic flow of single crystals, for instance, it has been observed that a simple pull applied to a cylindrical crystal of zinc produces a laminar shearing movement along the hexagonal base of the crystal, and here every ordered pair of initial and terminal positions will require a different trellis model

An extensive study has been made with the help of the trellis model of the behaviour of textile fabrics under simple pulls and this study which is published in a separate paper has fully confirmed the theoretical results discussed above

(2) The State of Strain under Complex Boundary Conditions

Consider a material which is held in grips and then subjected to mechanical actions through relative displacements of the grips The displacements of the grips impose at the boundaries between the material and the grips certain conditions which will set up throughout the material distributions of the stresses and strains These distributions can be calculated, in principle, by integrating the equation of motion of the material for the given boundary conditions, but, in practice, such a procedure is so complicated that only very simple cases can be calculated even if the equation of motion is known explicitly It is here that the trellis model can be used to provide a first-order approximation The method of obtaining such an approximation has been worked out for a variety of cases but the essential features of the model can best be appreciated in the special case in which the model gives an exact solution

Suppose the material is given in the form of a plane net in which the threads are inextensible, perfectly flexible and invariantly fixed to one another wherever they cross Let this net be held in grips, and the grips then displaced relative to one another in any way which leaves the threads in the plane of the net The resulting distribution of strains can then be predicted exactly from a suitably constructed trellis model

Let the net be laid out in some initial position with any number of grips attached to the net By an arbitrary displacement of the grips the net will then reach a terminal position with a certain strain distribution which we want to determine As the grips operate on the net by way of bundles of parallel threads which the grips hold we find that the edge threads of these bundles

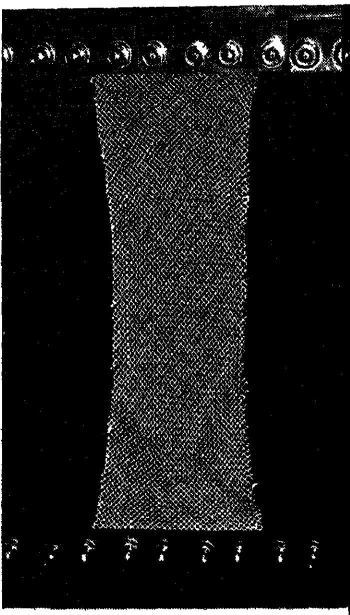

Fig 5 (a)

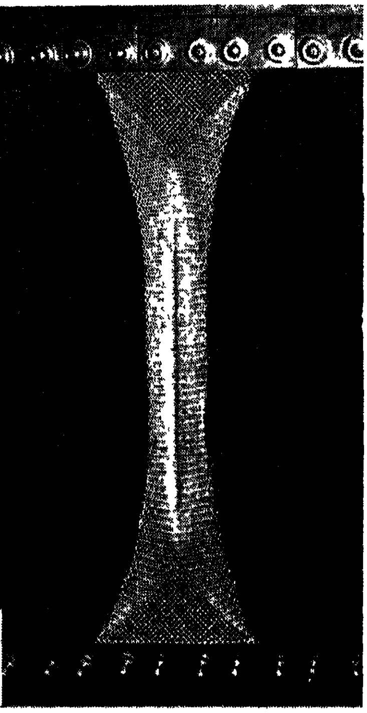

Fig. 5 (b)

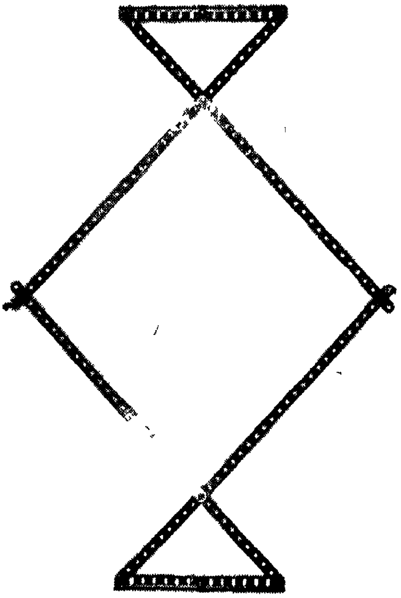

Fig. 6 (a)

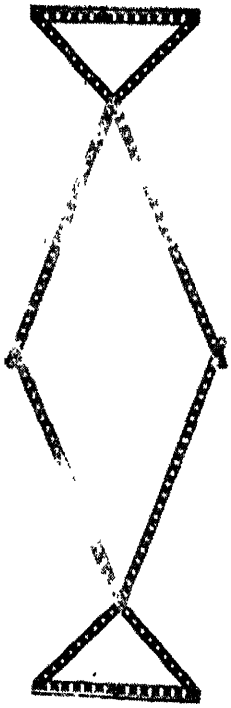

Fig 6 (b)

will separate from one another regions of different strains, however the grips may have been displaced. Moreover, each of the various regions so separated will be a region of homogeneous strain because of the assumed inextensibility and perfect flexibility of the threads. Hence, when the grips are fixed to the

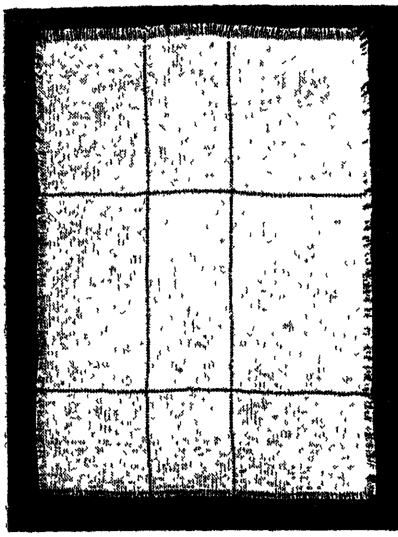

Fig 7 (*a*)

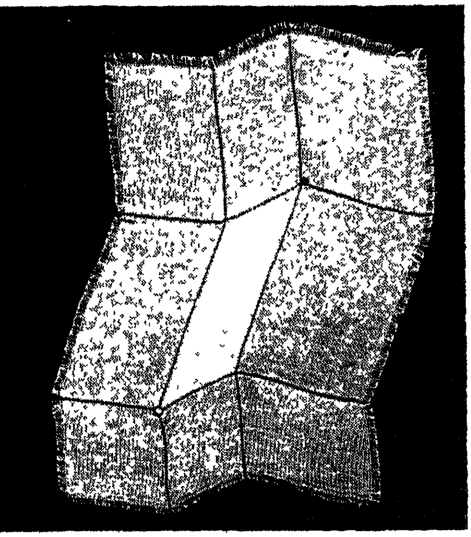

Fig 7 (*b*)

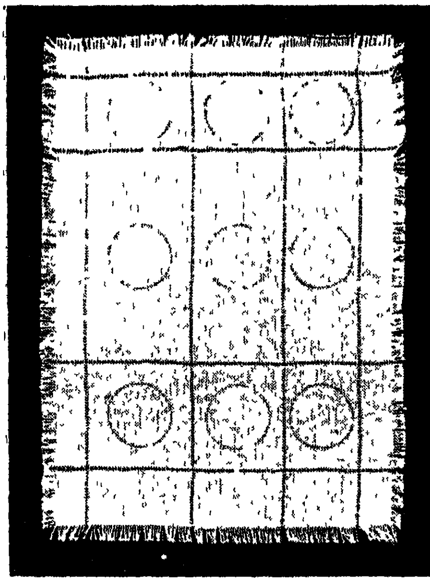

Fig 8 (*a*)

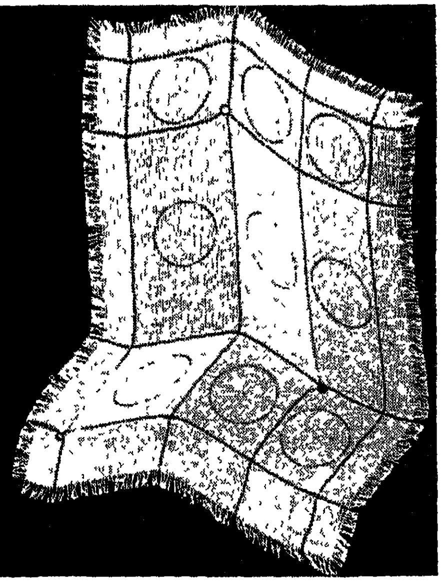

Fig 8 (*b*)

net in the initial position it is possible to mark out there a pattern of two intersecting series of parallel edge threads, and this pattern will divide the whole plane of the net once and for all into the different regions of homogeneous strain which can appeal in any terminal position The pattern in the initial position may be transformed into the pinpointed framework of a trellis model by substituting pinpointed pivots for the points at which the two series of edge threads intersect, and separate rigid rods for the various portions of the edge threads between two successive points of intersection. Fixing then the grips to the model and displacing them as for the net, we reach a terminal position for which the strain distribution in the model corresponds exactly to that in the net. In particular, the framework of the model in the terminal position will divide the plane of the model into different parallelogrammatic regions of homogeneous strain, and this division coincides with that produced in the net. In addition, each parallelogrammatic region of homogeneous strain will be bounded in the model by the rigid rods which form the sides of the parallelogram, and the directions of these sides coincide throughout the whole interior of the parallelogram with the directions of the threads of the net.

The application of the trellis model is not restricted to nets of inextensible and perfectly flexible threads but, in passing from such nets to plane sheets of woven and knitted fabrics, and finally to plane sheets of continuous materials of any kind, we find that the model will still exhibit the main features of the strain distribution and thus serve to give a first approximation, provided that we identify the threads of the net with the lines of zero elongations in the various materials, and determine these lines in preliminary experiments of simple pulls. The approximation will be particularly close when only infinitesimally small strains are imposed. In the special case of woven fabrics it has been shown that for wide ranges of mechanical actions the threads of the fabric are near to the lines of elongation, and this makes it possible to identity in many cases directly the threads of the net with those of the fabric. Figs. 5 (*a*) and (*b*) refer respectively to the initial and terminal positions of a specimen of fabric that is stretched between two parallel linear grips, and Figs. 6 (*a*) and (*b*) illustrate the relation between the strain distribution in the specimen and in the trellis model Figs 7 (*a*) and (*b*) refer to a stretching of a specimen between two pinpointed grips (drawing pins), and Figs. 8 (*a*) and (*b*) to a similar stretching between the three pinpoint grips The corresponding trellis models are exhibited in these Figures directly by marking in black the edge threads corresponding to the attached grips. Thanks are due to Mr G. E. Chadwick for the performance of the experiments.

ACKNOWLEDGEMENT

The author wishes to express his thanks and appreciation to Dr F T Peirce who inspired the development of Textile Mechanics from first principles and helped with the application of these principles to various engineering problems.

British Cotton Industry Research Association

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6—A TRELLIS MODEL FOR THE APPLICATION AND STUDY OF SIMPLE PULLS IN TEXTILE MATERIALS

By G. E. Chadwick, S. A. Shorter and K. Weissenberg

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ACKNOWLEDGEMENT.

This paper has been elaborated to provide a framework for the special problems of textile mechanics. The development of this branch of physical science owes much to the leadership of Dr. F. T Peirce, head of the Testing Department at the Shirley Institute, 1924-1945, and now Director of Textile Research, North Carolina State College, U S.A. The authors acknowledge their indebtedness to Dr Peirce for posing the problem and following the progress of the investigation with inspiration and enthusiasm.

INTRODUCTION AND SUMMARY

Textile fabrics present a behaviour of great complexity when examined under mechanical actions, such as occur in the various stages of manufacture, in practical use, and in the testing of the mechanical properties To unravel the complexities in such examinations the classical theory of mechanics has provided a mathematical form of analysis which has been greatly simplified by the introduction of a mechanical model This is referred to as a *trellis*, since it behaves like the well-known type of collapsible garden trellis, consisting of two sets of parallel rigid rods mutually pinpointed where they cross, and capable of expanding and contracting in certain directions without change in length or form of the rods. In an earlier paper K. Weissenberg* introduced the trellis model and developed a comprehensive scheme in which the classical theory and the theory of the model are united

The present investigation is limited to the behaviour under simple pulls of textile fabrics and other materials in the form of plane sheets, and for the convenience of the reader the trellis model is here derived in a simplified manner adapted to the special two dimensional case under consideration. Each sheet will be examined in two positions, in the *initial position* when the sheet is in its *natural state*, that is at rest and free from mechanical actions, and in the *terminal position* when it has reached some stressed and strained state under the action of the applied pull. Special methods were devised to reveal the stresses and strains under examination.

For the stresses, cuts were made in the sheet at various points, and in various directions, the amount of change (opening up or closing down) of a cut while the stress is maintained affording a very rough measure of the traction force across the cut In the initial position, corresponding to the natural state, the stress is zero and the cuts remain unchanged. In the terminal position, however, corresponding to the stressed state, changes can be observed in the cuts This is shown for the terminal position of a rectangular specimen of fabric by Figs 1(b) and 1(d) Fig 1(d) refers to a specimen which has been sewn into an endless belt and then stretched between two parallel rollers inserted in the belt The stress here produced is a *simple pull* lengthwise in the specimen, that is a stress homogeneously distributed over the whole area of the specimen with traction forces of finite amount across the widthwise cuts, and of zero amount across the lengthwise cuts This is revealed through the changes of the cuts being the same at different points of the sheet with a finite amount of opening of the widthwise cuts and zero opening of the lengthwise cuts By way of contrast Fig. 1(b) refers to a specimen which has been stretched between two parallel clamps firmly fixed

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* K Weissenberg, preceding *Memoir*.—See also *Arch d Sci Phys et Nat* 1935, 5 Par, Vol. 17.

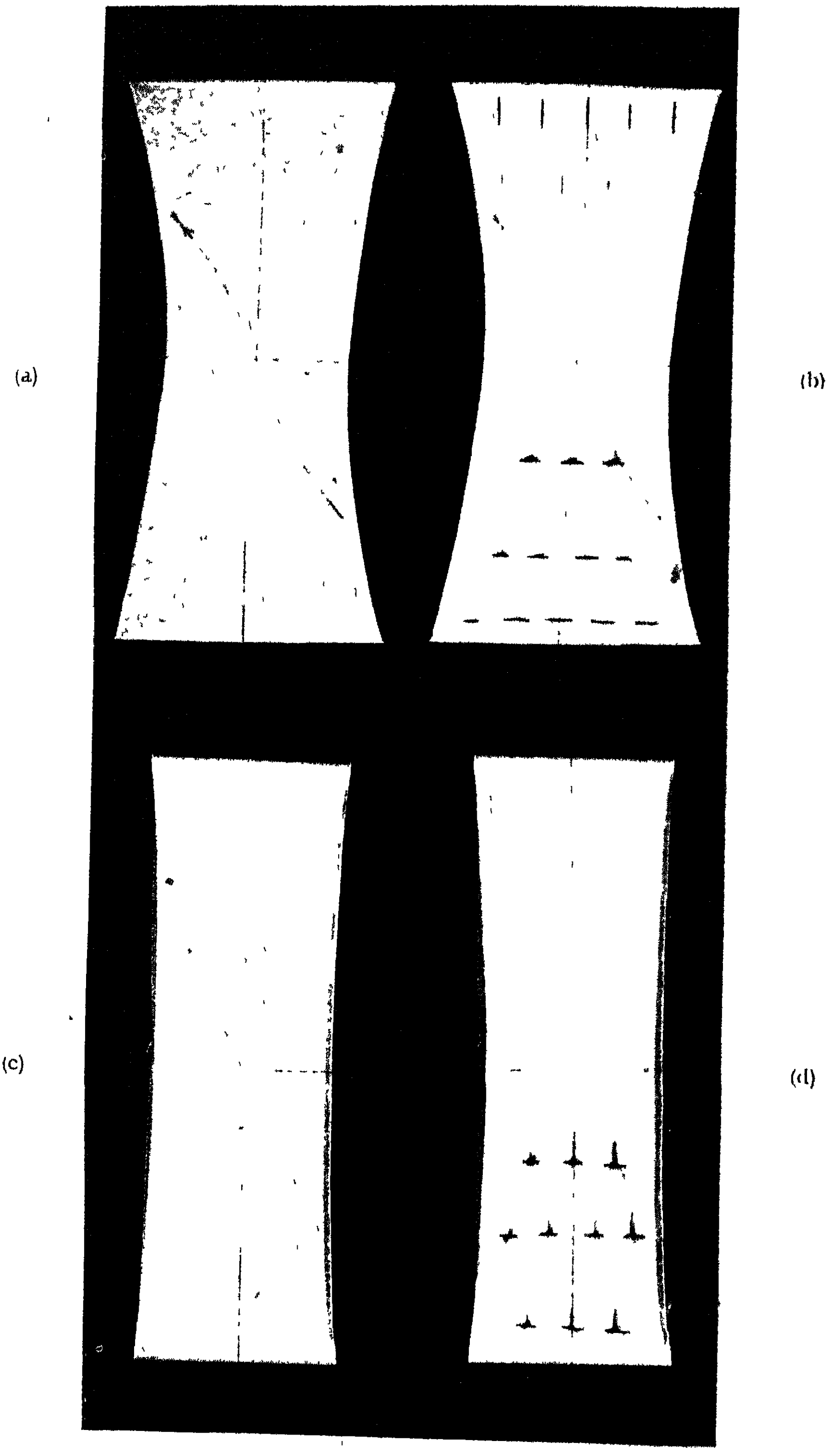

Fig 1

to the sheet. Here the stress is of a complex character, varying from one point to another, and having traction forces of finite amounts across widthwise and lengthwise cuts as seen in the corresponding changes in the cuts

For the strains, the geometrical changes were observed which occurred in the specimen in transition from the initial to the terminal position In principle it would be necessary to observe the strain separately at the various points of the specimen, but observation at one point will suffice since in the restricted investigation here under discussion the strain will be homogeneous over the whole area of the specimen The homogeneous strain produced by a simple pull manifests itself differently for the different elements in which we are interested In Fig 2(a)—(d) an illustration is provided for the initial and terminal positions of a specimen of fabric sewn into an endless belt and stretched between a pair of parallel rollers inserted in the belt. Figs. 2(a) and (b) refer to a specimen in which the direction of pull is along the weft, while Figs. 2 (c) and (d) refer to a biased specimen in which the warp makes an angle, termed *bias angle*, with the direction of pull. The manifestations of the

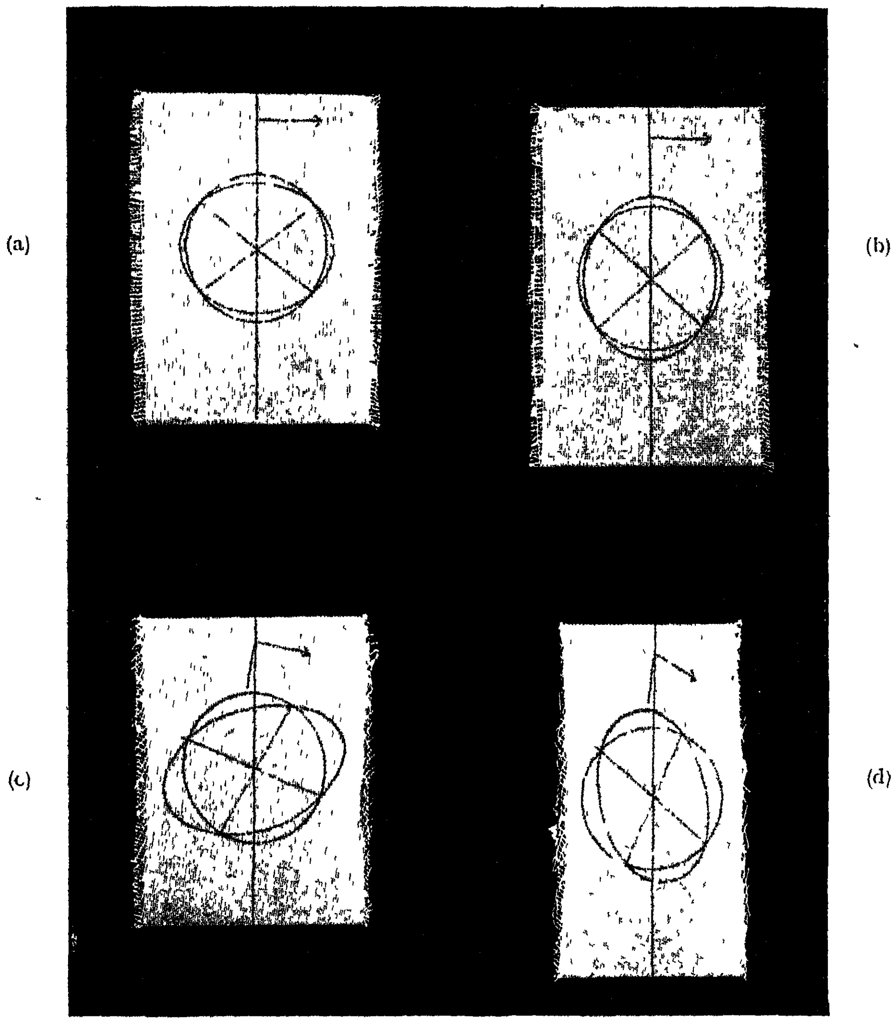

Fig 2

strain are studied here from four different aspects, discussed under the headings of shape, weave structure, strain quadrics and lines of zero elongation.

The shape of the belt between the pair of rollers is a rectangle, with sides parallel and perpendicular to the direction of the pull, and it is seen from Figs. 2(a)—(d) that for both specimens this rectangle changes its dimensions by suffering an elongation lengthwise to the direction of pull and a contraction widthwise according to a phenomenon known as the *Poisson effect*. It will be noticed that the contraction in the widthwise direction takes place in spite of there being zero traction force in this direction in a simple pull experiment.

Considering the weave structure, attention will here be focused on the changes occurring in the plane of the specimen, when straight lines are imagined to be drawn in this plane along the warp and weft threads. The photographs reproduced in Figs. 2(a)—(d) are in fact projections on to the plane, and the images of the threads shown there may be identified with the imaginary lines. The strain from the initial to the terminal position brings about some changes in the weave structure while maintaining invariant the straight linear form of the warp and weft lines, and the points of intersection between these lines. The changes in the structure are changes in the length, the density and the orientation of the warp and weft lines, and these changes depend on the properties of the specimen under examination and the amount and direction of the pull. For the specimen shown in Figs. 2(a) and (b) there is no change in the orientation of the warp and weft lines, but there is an elongation of the weft lines and a contraction of the warp lines, with a corresponding increase in the end spacing and decrease in the pick spacing. For the biased specimen, shown in Figs. 2(c) and (d), the warp and weft lines suffer not only changes in length and spacing, but also in their orientation to one another and to the direction of pull.

In order to study the homogeneous strain at a point systematically the classical theory introduced strain quadrics, that is curves of second degree, which are centred on the point and specify round the full circle of directions the changes in orientation and length of all lines irradiating from the centre. One quadric, termed *strain ellipse*, will change its form from a circle of unit radius in the initial position into an ellipse in the terminal position, with the main axes indicating there the directions of maximum changes in length, the major axis corresponding to the greatest increase and the minor to the greatest decrease. The other curve, termed *reciprocal strain ellipse*, changes its form conversely from an ellipse into a circle of unit radius, and the main axes of that ellipse are aligned in the initial position with the directions destined to suffer maximum changes of length, the minor axis now, however, corresponds to the greatest increase and the major axis to the greatest decrease. As the sheet suffers extensions in some directions and contractions in others, the strain ellipse and reciprocal strain ellipse will intersect and the pair of common diameters indicate in the two positions *lines of zero elongation**, that is lines in which there has been no change of length. Here the classical conceptions of the *main axes* of strain may be introduced. These axes, termed *major* for elongation, and *minor* for contraction, extend along the directions which suffer maximum changes in length and thus coincide in the two positions with the directions of the axes of the ellipses or, what amounts to the same, with the directions of the bisectrices of the angles between the lines of zero elongation. Figs. 2(a) and (b) illustrate a special case of strain, termed *pure strain*, where the main axes of strain have the same orientation in both the initial and terminal positions. Figs. 2(c) and (d) illustrate a general case, where the orientation of the main axes changes from the initial to the terminal position, and the strain contains a corresponding rotation of the sheet as a whole, in addition to the pure strain.

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* In the classical theory, attention has already been drawn to the lines of zero elongation (see for instance W. J. Ibbetson, Mathematical Theory of Elasticity) and G. I. Taylor was the first to use these lines in an analysis of three-dimensional strains produced in the plastic flow of single crystals (see *Proc. Roy. Soc. A*, 1923, Vol. 102, and 1926, Vol. 111.)

When, finally, it is required to consider the strain in terms of the lines of zero elongation, it will be noted that these lines divide the full circle of directions into two complementary pairs of sectors. One pair, centred on the major axis of strain, decrease from the initial to the terminal position and contain all lines which suffer an elongation, while the other pair, centred on the minor axis of strain, increase from the initial to the terminal position and contain all lines which suffer a contraction. To specify the directions of the lines of zero elongation it has been found convenient to do this with the help of two angles One, termed *opening angle,* corresponds to the decreasing pair of sectors formed by the lines, and the other, termed *angle of evasion,* corresponds to the acute angle formed by the direction of the pull and the direction of maximum elongation, that is between the major axis of stress, and the major axis of strain In Figs 2(a) and (b) it is seen that the opening angle between lines of zero elongation corresponds to the pair of sectors which contains the direction of pull The angle of evasion is here zero in both positions as the direction of the pull, that is the length direction of the specimen, coincides with the major axis of strain In Figs 2(c) and (d) the opening angle again contains the direction of pull Here, however, the angle of evasion is not zero and shows the discrepancy between the direction of pull lengthwise to the specimen, and the direction of the major axis of strain along which the maximum elongation occurs The discrepancy decreases from the initial to the terminal position. From all the Figs 2(a) to (d) it can be seen that lines of zero elongation change only their orientation, but retain as invariants from the initial to the terminal position, the length, the straight linear form, and the point of intersection. Thus, the strain of the sheet produces in the lines of zero elongation the same changes as in the rods of a collapsible trellis, and this fact makes it possible to represent the strain of the sheet by a trellis model.

The stresses and strains revealed in a sheet of fabric are subjected to certain fundamental laws which have been formulated in the classical theory of mechanics It has been shown in the preceding paper how these laws impose on the freedom of movement certain restrictions which are known in the theory as *Lagrange forces of restraint,* and are incorporated into a mechanical model of the type of a *trellis* The framework of the model consists of two intersecting series of parallel rigid rods which extend along the lines of zero elongation and are pivoted to one another by the insertion of pin-pointed joints at the crossing points of the rods It is necessary in principle to equip the framework of the trellis with a disposition of masses, and of elastic and frictional resistances' (springs and dashpots say), but this additional equipment need not be specified here and will be left undeterminate.

It can be shown that the trellis mechanism so constructed will in fact guide the sheet along the movements allowed by the laws of the classical theory and will, at the same time, prevent the sheet from movements in any way contrary to the laws Any pattern imprinted on the trellis in the initial position will then change through the trellis mechanism to the corresponding pattern in the terminal position as required by the theory, so that the trellis can be made to serve as a model for the strain produced in the sheet provided an adjustment is made to the conditions of the experiments, such that the series of rigid rods of the trellis extend in the initial and terminal positions along the lines of zero elongation Because of this adjustment the lines of zero elongation and the rigid rods of the trellis will also be referred to as *trellis lines.* It will be noted that in the model the distances between parallel rods can be chosen arbitrarily and that only two pinpointed joints are required on each rod The model can in fact be simplified to a representative rhombohedral frame, consisting of four rigid rods pivoted to one another at the corners of the *rhombus* As the sheet is strained from the initial to the terminal position, the framework of the trellis performs a movement in a lazy-tong fashion with one pair of angles in the rhombus decreasing and the other increasing. With reference to the Figs 2(a)—(d) special attention is drawn to the different orientations in the initial and terminal positions of the lines along the yarn threads which characterise the structural network of the fabric, and the lines of zero elongation which characterise the structural network of the trellis model associated with the fabric

The classical theory and the trellis model discussed above apply primarily not to real materials but to ideal media which satisfy exactly the laws of the theory. It is, however, possible to fit an ideal medium as closely as may be to any given real material, and a more detailed investigation reveals that one obtains an almost perfect fit for every given woven or knitted fabric if the fabric is represented by a network of two intersecting series of parallel straight lines drawn in the plane of the fabric along the yarn directions Having fitted an ideal medium to a real material one can apply the classical and trellis theories as explained above

There are many advantages in using the theory of the trellis model as a supplement to the classical theory as will be seen from the considerations given below

In the experimental study of the behaviour under simple pull of textile fabrics and other materials in sheet form, rectangular specimens were cut out in various directions Each specimen was subjected to a series of simple pulls of increasing amounts in a direction lengthwise to the rectangle For each experiment in the series, the behaviour of the specimen was specified by the strain from the initial to the terminal position To make the specification comprehensive there was imprinted on the specimen in the initial position a set of markings which was sufficiently complete to reveal by its initial and terminal patterns all the characteristics of strain with regard to the yarn structure, the classical theory and the trellis model, as explained with reference to the shape, the weave structure, the strain quadrics and the lines of zero elongation

Considerable difficulties arise in the task of imposing on a given sheet of material homogeneous states of strain, such as correspond to the action of simple pulls, and special devices had to be developed for this purpose

In the ordinary tensile testing of cloth, a rectangular specimen of th material is fixed widthwise in a pair of parallel clamps, and these clamps are then pulled apart in order to produce an extension in the length of the specimen. An investigation of the results obtained reveals that the state of stress imparted to the specimen under these conditions differs considerably from the intended one of a simple pull and that a corresponding difference is observed in the state of strain This may be observed experimentally by making small cuts in the material at various points and observing the opening or closing of the cuts with the applied pull The trouble is due to the fact that the material is tested under boundary conditions which are incompatible with the imposition of the intended stresses and strains, since a simple pull on the specimen requires that the elongation of the specimen lengthwise should be accompanied by a contraction widthwise, whilst the fixing of the specimen to the grips creates boundary conditions under which the widthwise contraction is resisted This restraint is particularly pronounced in the immediate vicinity of the grips, and the increasing freedom from the restraint in regions remote from the grips leads to a heterogeneity in the imposed strain, of which the most obvious sign is the waisting of the specimen

The requirements of a simple pull may, however, be attained by means of two special kinds of grip termed, respectively, roller grips and trellis grips In the roller grips an endless belt of the specimen is prepared an mounted on two rollers which are aligned at right angles to the length of the specimen By this means the specimen has sufficient freedom to contract freely on the rollers during the stretch. The trellis grips have been developed from the trellis model and are not subject to some of the limitations of the roller grips. It has been shown that any desired state of strain may be produced in a material by performing a trellis-like movement with the pin-pointed network of lines of zero elongation Accordingly, the strain may be produced by performing a similar movement with trellis grips which consist of inextensible linear grips fixed along the directions of the lines of zero elongation of the fabric and pivoted to one another at their crossing places Two such trellis grips, termed, respectively, "angle" and "parallelogram" grips have been devised. The angle grip conforms to one pair of sides of the parallelogrammatic frame and consists of two clamping arms which are pivoted to one another by a hinge at one end so that the angle between the arms may be varied freely. The parallelogram grip conforms to one pair of parallel sides of a parallelogrammatic frame and consists of two parallel clamping arms which are pivoted to two cross rods so that the angle between the arms and rods may be varied arbitrarily. It can be shown experimentally that both the states of stresses and strains in the ordinary parallel grips of a tensile tester are heterogeneous whereas in roller, angle and parallelogram grips they are homogeneous[*] provided the grips are set in the directions of the lines of zero elongation in the initial position In all trellis grips the specimen should have its free edges along the direction of pull since the force acting across such boundaries is zero for a state of simple pull.

The angle grip is a particularly simple means of applying homogeneous stresses and strains to fabrics and it may be used in conjunction with a Goodbrand cloth tensile tester to give the breaking load of a strip of fabric Another practical application of the grips is that they may be used to apply a ballistic fatigue treatment to coated fabrics to determine the resistance of the coating to destruction under repeated stresses and strains.

The trellis model is of particular value in the study of the behaviour of textile fabrics under the action of a simple pull This is readily visualised and demonstrated by means of an actual model constructed from four strips of "Meccano" jointed together to give a rhombus

In the initial position the rhombus may be set with the sides parallel to the initial directions of the lines of zero elongation and the joints of the model coincident with nodal points of the material. The model should be operated by stretching it in the direction of pull to the amount actually observed in the specimen[†] In such an experiment the behaviour of the model shows directly the various characteristics of the strain from the initial to the terminal position The characteristics of pinpointing and linearity are seen for the trellis lines in the maintenance of their points of intersection and of their straight linear form, whilst the characteristics of the Poisson effect are recognised by the changes in length parallel and perpendicular to the direction of pull (that is lengthwise and widthwise in the specimen) these changes being coupled For a general case, when the diagonals of the rhombus are orientated arbitrarily relative to the direction of the pull, the model appears to execute an *evading action* since the maximum elongation occurs in a direction which is at an angle to that of the pull The strain here is compounded of a pure strain extending its main axis along the diagonals of the rhombus and a rotation which turns these diagonals round and brings the direction of maximum elongation nearer to that of the pull For a special case when one of the diagonals of the rhombus coincides with the direction of the pull, the model will suffer a strain which is a pure one free from evasion and rotation

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[*] The state of stress or strain is not homogeneous if the initial angle between the grips does not correspond to the appropriate angle between the lines of zero elongation. When the angle between the clamps is less than that between the lines of zero elongation waisting occurs , when greater, buckling occurs

[†] This mode of operation ensures that the trellis lines coincide with the lines of zero elongation in the initial and terminal positions

The experiments on specimens of fabric show that the behaviour of the specimens under simple pull corresponds in all the characteristics of strain to that of the model It has been found that under a simple pull the component threads of a fabric retain their nodal points intact, that is they do not glide over one another and are apparently pinpointed to one another Further, under a simple pull all specimens of textile materials undergo a linear change which is recognised in the pattern of markings by the straight lines remaining straight and the curves of second degree remaining of second degree. The Poisson effect with and without evading action shows up rather strikingly

If the material in its natural state is isotropic the model would be so orientated in the initial position that one diagonal of the rhombus is in the direction of the pull and the other at right angles to it. Here the belt suffers a pure strain with maximum extension occurring lengthwise and maximum contraction widthwise in accordance with the Poisson effect This was confirmed in experiments on isotropic sheets of materials such as rubber, Cellophane, polyvinyl chloride, etc. If, on the other hand, the material in its natural state is anisotropic, and this is the case for all woven and knitted textile fabrics, then the relative orientation of the model to the pull is different for various directions of pull, i.e for various bias angles. For an arbitrarily chosen bias angle the diagonals of the rhombus will be inclined to the direction of the pull, and the results obtained here will conform to those of the model in the general case For a specimen cut at an arbitrarily chosen bias angle of nominally $22\frac{1}{2}°$, the belt suffers a compound strain extending lengthwise and contracting widthwise in accordance with the Poisson effect, and evading the direct action of the pull, as a circle drawn on the fabric extends into an ellipse in a direction different from that of the pull In this evading action, the belt is seen to suffer a pure strain with maximum elongations and contractions occurring in directions oblique to the length and width directions of the specimen, and to suffer, in addition, a rotation which carries parts of the specimen over the rollers, in spite of the strong frictional forces present, one free edge of the front sheet of the belt moving upwards over the rollers, and the other free edge of this sheet moving downwards For specially selected bias angles, the model in the initial position is so orientated that one of the diagonals of the rhombus is in the direction of the pull and the other at right angles to it The results obtained will here conform to those of the model in the special case, and this was confirmed in experiments when the specially selected bias angles were 0° and 90°, and for woven fabrics in addition, 45° approx

The model accounts for the behaviour of the specimens not only in the qualitative way discussed above, but also in a quantitative way for all numerical characteristics of the strain This is exhibited in tables where the numerical values of strain are recorded with respect to the yarn structure, to the classical theory and to the trellis model

The practical value of the trellis model is considerably enhanced still further by the empirical fact that in all the specimens of textile fabrics under examination, the trellis characteristics calculated for the initial position vary only slightly with the amount of pull, so that the same trellis model may be used in all experiments in which a specimen of given bias angle is stretched by various amounts of pull It must, however, be emphasised that caution is needed in generalisation of the empirical fact to other materials and other actions In theory the characteristics of the trellis model must be adapted separately for each pair of initial and terminal positions, and only a separate investigation can show to what extent the same characteristics apply to more than one pair of positions.

The trellis model has a certain structural significance for textile fabrics and this is brought out in the association between the structural elements of the model and those of the fabric. The pinpointed joints of the model have already been identified with the nodal points on the fabric and it thus remains to investigate the relation between the rigid rods and the yarns of the fabric, the rods being represented by the trellis lines and the yarns by lines drawn along the threads.

For an ideal fabric constructed from rigid threads, there would be a coincidence between the trellis lines and the lines drawn along the thread directions The real textile fabrics deviate from the ideal to a greater or less degree and this modifies the kind and degree of association, and makes it dependent on the particular conditions of the experiment. It suffices, however, to consider the initial position only, since the association in the terminal position is similar The fabrics have conveniently been divided into two types, woven and knitted fabrics, and for each the experimental conditions were varied with regard to the direction of the pull (bias angle)

For all samples of woven fabrics the extensibility under pull in the various directions shows a characteristic pattern The pattern is symmetrical to the warp and weft directions and the value of the extensibility changes with the bias angle in a wave-like form (four-leaf clover) passing through sharp troughs with minimum values at the bias angles corresponding to the directions of warp and weft, and passing through flat crests with maximum values at bias angles near to, or coinciding with, the bisectrices of the angles between the warp and weft directions The full circle of bias angles may thus be divided roughly into two complementary sets of sectors, corresponding respectively to the troughs and the crests of the wave One set of sectors with large values of extensibilities (corresponding to the flat crests of the wave) consists of four broad sectors which are centred on the bisectrices between the warp and weft, and throughout these sectors the trellis lines are almost coincident with the lines drawn along the warp and weft threads. The complementary set of sectors with small values of extensibility (corresponding to the sharp troughs of the wave) consist of four narrow sectors which are centred on the warp and weft directions, and here the trellis lines deviate considerably from the lines drawn along the warp and weft threads The deviation increases to a maximum value as the direction of the pull approaches the direction of warp or weft. On either side of the maximum deviation there is a well-defined association in which one trellis line is near the warp and one near the weft. As the direction of pull passes over a yarn direction there is a change in the mode of association so that the trellis line previously associated with the weft will now become associated with the warp, and vice versa At the maximum deviation the trellis lines are symmetrically orientated to the warp and weft directions, and the association is arbitrary This association has been found to apply to a wide variety of woven fabrics of different weaves and constructions

For knitted fabrics only one sample has been investigated Here the extensibility under pull in the various directions shows a pattern which again is symmetrical to the yarn directions One of these directions, that of the wales, corresponds to a minimum of extensibility, and here there is a close association to the one or other of the trellis lines similar to that found for the yarn in a woven fabric The other yarn direction in the knitted fabric, that is the courses, corresponds to a maximum extensibility, and therefore shows only an incidental association with the trellis lines

The experimental results suggest that in any material which varies in extensibility with the direction of the pull there is an appreciable association between the direction of minimum extensibility and the trellis lines representing the lines of zero elongation This structural significance of the trellis lines is not restricted to the actions of simple pulls but holds good for a variety of mechanical actions though not for all of them

THE EXPERIMENTAL TECHNIQUE

The experimental conditions have been limited as follows:—

Materials All materials were selected in the form of plane sheets and samples were free from obvious defects In general the experiments have been made on woven and knitted textile materials of various structures but some preliminary tests were also made on sheets of rubber, leather, Cellophane, etc

Mechanical Actions The materials were subjected to simple pulls and the magnitude of the pull was restricted to a range of values between zero and a value below the critical point at which breakage or disintegration of the structure occurred.

Time Factor. To reduce any possible time effect, the terminal state corresponding to any applied simple pull was taken to be that after an approximately static state of equilibrium was reached. For the textile specimens examined this time interval was about 2 minutes The experiments were carried out in steps as detailed below

(1) Preparation, Marking out and Photographic Recording.

The experimental results relate to samples of a representative selection of textile fabrics which have been subjected to simple pulls of varying magnitude at different bias angles. Table I gives the structural details of the fabrics and accords to each a reference label, A, B, etc. Fabrics A, B, C and D were chosen because they had a fairly open structure and the effects of the various structural factors could be noted Fabric E was chosen because of its close structure. Fabric F was chosen to represent knitted fabrics and fabrics G to K as representing different fibres

For each fabric oblong specimens 20 ins long by 5 ins wide were cut from the bulk sample and simple pulls were applied lengthwise to these as described below. In principle a complete range of bias angles extends over 180° but by virtue of the structural symmetry of the fabrics about their main yarn directions (warp and weft for woven fabrics, wales and courses for knitted fabrics) a range of 90° from one yarn direction to the other could be taken as adequate The conventions are that the lengthwise direction of the specimen is the direction of the simple pull and that the acute angle between this direction and the warp direction is the bias angle. All angles are measured positively in a clock-wise direction as viewed from the face of the fabric on which the markings are made In the present investigation the bias angles were chosen with negative values For the samples A and F specimens were cut out at bias angles of 0°, −11°, −22½°, −45°, −67½°, −79°, and −90°, whilst for the other samples specimens were cut out only at the arbitrarily selected bias angle of −22½°, typical of the general case

Each specimen was carefully freed from wrinkles and held firmly between two rings of cardboard A circle 4 ins diameter was then marked in Indian ink in the centre of the specimen and the warp and weft directions were marked by lines drawn through the centre of the circle, an arrow head being attached to the warp line to serve as an identification mark In addition a line was drawn through the centre parallel to the length of the specimen to indicate the direction of the intended pull The marked specimens were then mounted in appropriate stretching frames as explained below, in which the magnitude of the simple pull could be varied as required For photographic recording of tests made when using roller grips, a Leica camera was held in front of the specimen by means of a steel gantry bolted to the cloth stretching frame. The gantry was arranged so that the camera could be placed in any position in a vertical plane 56 cm. from the front of the specimen and by means of a slotted member provision was made for moving the camera in a vertical direction to be in line with the centre of the circle marked on the specimen The camera was set at F.9 0, $\frac{1}{20}$th second, and Kodak R 50, 35 mm. recording film was used as the sensitive material. A single Matelux lamp and reflector placed 5 ft. from the specimen and giving fairly flat lighting were found to give well-exposed negatives. An exposure was first made with the specimen held loosely in the grips and the centre of the camera lens in line with the centre of the marked circle. The specimen was then stretched by the frame and, after re-aligning the camera, the film was exposed and the reading of the spring balance noted. The procedure was continued so that a series of exposures of increasing amounts of strain were obtained.

For the trellis grip tests a similar photographic procedure was adopted with the specimen placed on a horizontal plane and the camera held vertically above it by means of a rigid tripod.

The film was developed for 4 minutes in I.D 2 developer and after processing and drying a quarter-plate enlargement of the markings on the cloth was made from each of the negatives and results were computed from the enlargement Considerable care was needed in computing the results and for this purpose a specially graduated small-scale protractor, steel rule and dividers were used Measurements of angle are correct to within 1°, of length to 0 01 inch

(2) Stretching Frames for the Production of Simple Pulls and the Mounting of the Specimens in the Frames.

The imposition of simple pulls meets with considerable practical difficulties which make it necessary to construct special stretching frames for the purpose and to develop appropriate schemes for mounting the specimens in the frames.

If one of the specimens of the material is mounted lengthwise in a pair of parallel clamps, such as are used, for example, in a cloth tensile testing machine, and these clamps are then separated in the ordinary way by increasing the distance perpendicular to the edges of the clamps, it is found that the state of stress imparted to the specimen differs considerably from that of a simple pull, particularly in the neighbourhood of the clamps, although only a pull lengthwise to the specimen is applied. The trouble is due to the fact that the material is tested under boundary conditions which are incompatible with the imposition of a simple pull. It follows from the theory that the imposition of a simple pull lengthwise to the specimen is compatible only with a homogeneous state of strain in which an elongation of the lengthwise direction is coupled with certain changes in length and in orientation of the widthwise direction, in accordance with the Poisson Ratio and the evading action present The fixing of the material in the clamps introduces a restraint in the widthwise direction and the effect of this restraint increases towards the boundaries of the specimen at the clamps till, in the immediate neighbourhood of these boundaries, all changes in length and in orientation of the widthwise direction are completely inhibited. Thus, the boundary conditions prevent the specimen from executing freely the required changes, and a pull on the clamps will induce highly heterogeneous and complex states of stresses and strains instead of the intended homogeneous ones which correspond to a simple pull.

Figs. 1(a) and 1(b) (see Introduction) show the result of an experiment carried out to illustrate the above-mentioned heterogeneity and the complexity of the states of stress and strain. A specimen of poplin fabric (E of

Table I, 20″×5″) was cut at an angle of 45° to the warp direction and fixed firmly in a pair of parallel grips of the usual type of cloth tensile testing machine Under a lengthwise pull the specimen stretched and assumed a waisted form as shown in Fig 1(a) The state of strain is heterogeneous, varying lengthwise and widthwise as can be seen from the distortion of the straight line drawn parallel to the warp threads of the specimen. Similarly the state of stress is heterogeneous, and to show its variation over the specimen small cuts were made at various places, the opening out of a cut indicating a positive stress component (pull) in a line at right angles to the line of the cut, and the amount of opening out affording a very rough measure of the magnitude of the stress component The cuts were made as short as practicable in order to minimise any interference with the stress distribution. In the upper half of the specimen lengthwise cuts were made to indicate widthwise stress components, and in the lower half widthwise cuts to indicate lengthwise stress components. Fig 1(b) shows the results obtained On considering the cuts in the upper half of the specimen, it will be seen that near the grip there is an appreciable widthwise stress component opening the cut, arising, of course, from the fact that grips prevent the widthwise contraction This component diminishes towards the middle of the specimen as is shown by the diminished amount of opening of the cuts, the line of cuts nearest the middle of the specimen being scarcely visible in the photograph, the reason for this diminution being the increasing freedom of the specimen to contract widthwise In the lower half of the specimen widthwise cuts were made to indicate lengthwise stress components, and it will be evident that these increase towards the middle of the specimen A similar stress distribution may be observed for a sheet of rubber.

The difficulties of adapting the boundary conditions of stretching frames to the requirements of the simple pull have been overcome by the development of two special kinds of grips* referred to, respectively, as "*roller grips*" and "*trellis grips*"

Roller Grips In order to adapt the boundary conditions to the requirements of the simple pull a pair of grips termed roller grips have been used in which the specimen can be mounted so that it has sufficient freedom to take up any state of strain required by the simple pull. The roller grips consist of two cylindrical steel rollers (mild steel rods of ⅜″ diameter) which were connected to the clamps of a cloth stretching frame such that the axes of the rollers were parallel to one another and aligned in a direction perpendicular to that in which the clamps are separated in an ordinary tensile test The tensile testing machine used was of the vertical type† with a fixed clamp at the lower end, and a movable clamp at the top connected directly to a spring balance which in turn was connected to a lever By this construction any force applied to the lever was communicated to the grips and indicated on the spring balance A photograph of the machine is shown in Fig 3

To mount a specimen in the roller grips it was first stitched at right angles to its length to give an endless belt 16″ long The two roller grips were then inserted in the belt, and fixed in the clamps of the testing machine Finally, the belt was stretched by separating the clamps through a force applied to the lever.

It is important that the belt of material can freely contract widthwise on the rollers during the stretch and it is advantageous, although in most cases not necessary, to reduce the friction of the specimen against the rollers by lubricating them with chalk, graphite, or the like, or by rotating them during the experiment

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* In addition, a swivel grip was suggested, which functioned in a similar manner to the angle grip described below but relied upon the pinpointing in the material to provide the conformity with the trellis motion

† The vertical type was chosen in preference to a horizontal one since the frictional forces operating are in general less

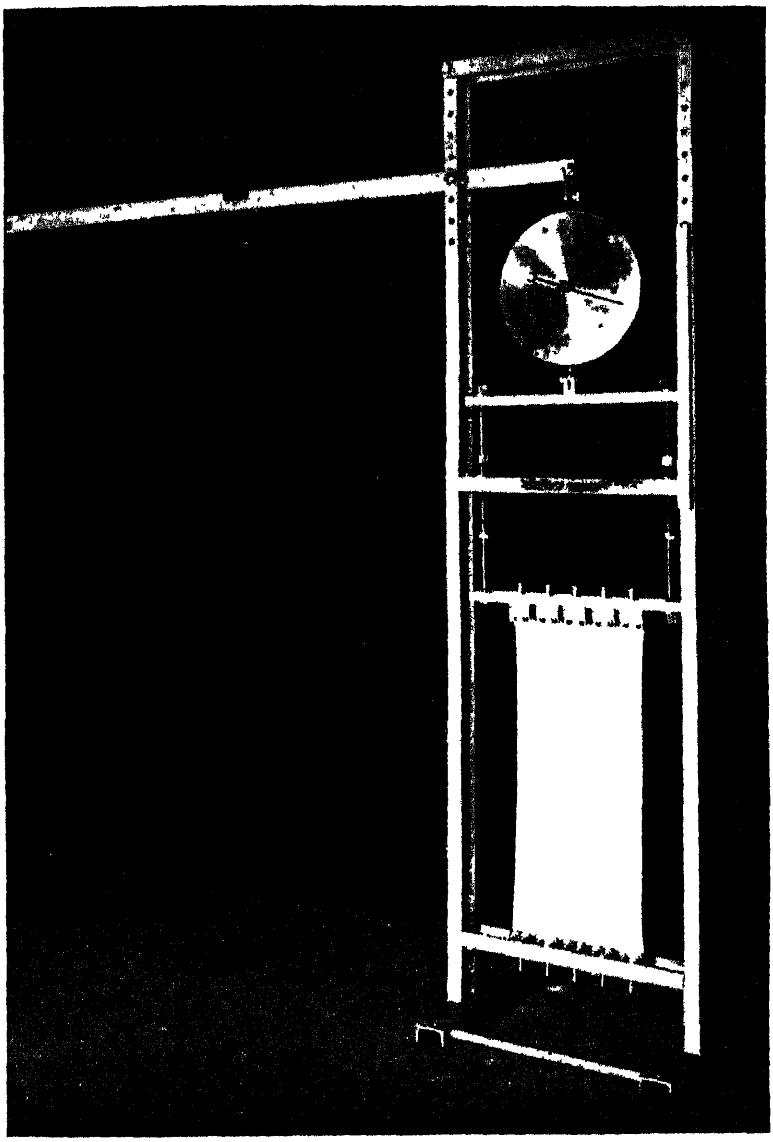

Fig 3

That the roller grips in fact produce in a correctly mounted specimen a state of stress which is appreciably near to a simple pull[*] is shown in Figs 1(c) and 1(d) which exhibit the same material as Figs 1(a) and 1(b) It may be seen in Fig 1(d) that in accordance with the requirements of a simple pull the stress is effectively homogeneous over the whole strip of material with regard to the length and widthwise components, and also that the widthwise stress component is practically zero*.

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[*] The roller grips are not ideally suited to produce a simple pull although they are quite good for most practical purposes It should be noted that each sheet of material has a finite thickness, and this thickness is compressed on the rollers since the material is pressed against them during the stretch The state of stress of the material on and near to the rollers will thus not correspond to a simple pull, and the state of strain will correspondingly differ from the ideal one However, the discrepancy is in general small, particularly when sufficiently thin sheets of material are used The roller grips possess the disadvantage that under considerable pull "gaping" of the seam occurs and introduces distortion

Having ensured that the roller grips produce the intended state of stress, namely a simple pull lengthwise to the specimen, the states of strain associated in the equilibrium with the simple pulls may now be considered It is found that for all specimens of textile fabrics and all amounts of pulls applied, the *state of strain is practically homogeneous* over the whole area of the specimen. Experimental evidence for the homogeneity of the state of strain is easily collected It can be seen for instance, that the simple pull applied to a specimen as shown in Fig 1(c) produces a terminal position with a state of strain as shown in Fig. 1(d), in which the specimen remains practically free from buckling and waisting, and in which a straight line drawn warp-way on the specimen in its initial position, has remained straight in the terminal position. Full proof of the homogeneity of the state of strain was obtained by examining closely the projections of the warp and weft threads on the plane of the fabric. These projections approximate in the initial and terminal positions to a network of two intersecting series of parallel and equidistant straight lines, and this fulfils the necessary and sufficient condition for the nodal points of the specimen to suffer a state of strain that is practically homogeneous.

Thus the roller grips have been shown to produce states of stresses and strains that are practically homogeneous over the whole area of the specimen, and conform to the requirements of a simple pull lengthwise of the specimens

Trellis Grips † In the Introduction it has been shown that any desired state of strain may be produced in a material by performing, from its initial to its terminal position, a trellis-like movement with the pinpointed network of lines of zero elongation Accordingly, the desired state of strain may be produced experimentally by performing a similar movement with "trellis grips," i.e a network of inextensible linear grips which are fixed in the material along the lines of zero elongation, and pinpointed to one another where they cross

Trellis grips are thus essentially a means for producing a certain state of strain However, if it is known from preliminary experiments with other stretching frames which state of strain corresponds to the desired state of stress, then this state of stress can be produced by making the trellis grips conform to the corresponding state of strain In the particular case of a simple pull, for instance, preliminary experiments on roller grips (see Fig 1(c) and 1(d)) show that the corresponding state of strain is homogeneous and conforms therefore to a certain network of straight lines of zero elongation, which remain straight when the material changes from the initial to its terminal position If, then, a pinpointed network of rigid grips is constructed that corresponds exactly to the network of the lines of zero elongation, and if this is fixed to the material in its initial position, then it is possible to impose on the material the correct strain required for the simple pull by expanding the network of grips trellis-like

For materials, such as textile fabrics, which have sufficient rigidity the trellis grips can be simplified considerably. It suffices merely to replace the network of grips by one parallelogrammatic pinpointed frame and to fix the specimen only to two sides of that frame, provided that the boundary of the material which is free from the grips runs parallel to the direction of the pull Such a "free" boundary is compatible with a simple pull since the components of a stress perpendicular to this direction are zero‡.

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* Note that the widthwise stress component is practically zero, but that the widthwise strain component conforms to the Poisson contraction and is appreciably different from zero

† British patent No 590639

‡ In the roller grips the belt has also free boundaries parallel to the direction of the pull

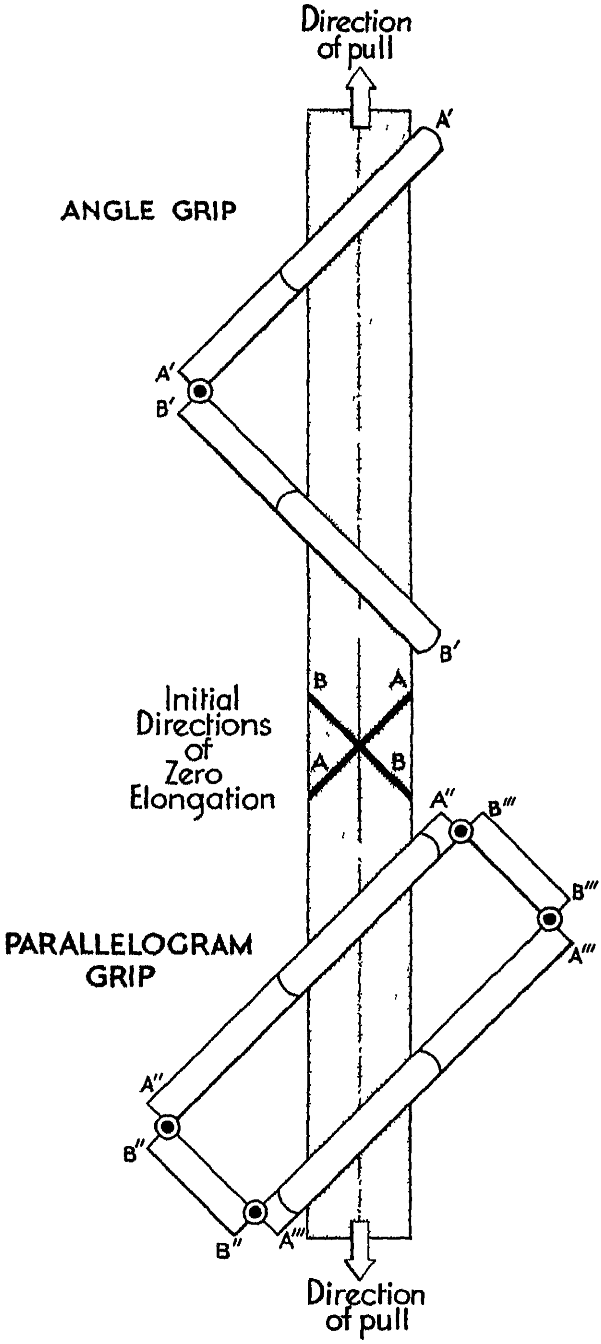

Fig 1

Thus for the present experiments two particularly convenient types of trellis grips were developed One type, termed "angle grip," conforms to one pair of intersecting sides of the parallelogrammatic frame and consists essentially of two clamping arms which are pivoted on one end by a hinge such that the angle between the arms can be varied freely.* The arms were made each of a couple of $12\frac{1}{2}'' \times 1\frac{1}{4}'' \times 3''$ mild steel bars bolted together by $\frac{3}{8}''$ Whitworth bolts and the angle between the arms could be adjusted and locked at any angle by a $\frac{3}{8}''$ rod and collar system connected to the arms at the ends remote from the hinge The hinge was arranged to be in the line of gripping of the specimen

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* It must be noted that the angle between the grips is complementary to the opening angle of the trellis, as the latter has been defined as the angle which decreases as the stretch proceeds

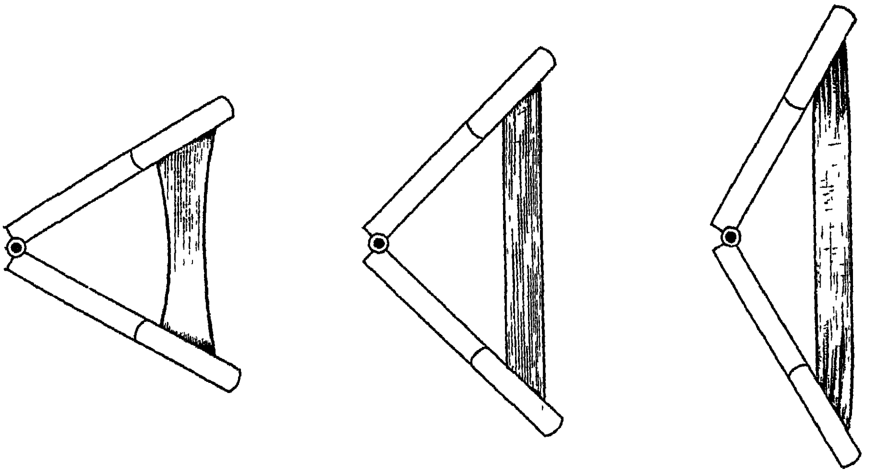
The second type, termed "parallelogram grip" conforms to one pair of parallel sides of the cell and consists essentially of a pinpointed parallelogram formed by two parallel clamping arms which are pivoted to two parallel cross rods such that the angle between the arms and the rods can be varied arbitrarily. The clamping arms were built as described above and the adjustment and locking of the angle between the arms and the rods was by means of the four bolts required to hold the framework together

The mounting of the specimens in the trellis grips (angle- and parallelogram-grips) requires special attention As already mentioned earlier in this section the correct mounting of a specimen in a trellis grip requires a knowledge of the trellis of lines of zero elongation in the initial position for the strain which is associated with the simple pull under consideration. This information may be obtained from preliminary experiments with roller grips. Fig 4 shows the details of a correct mounting A specimen is taken in its initial position and marked with the direction of the simple pull and the directions of the two lines of zero elongation. The specimen is then mounted and fixed to the angle grip in such a position that the members of the grips marked A′A′ and B′B′, are respectively parallel to the directions of zero elongation marked AA and BB Similarly, in the parallelogram grip the members of the grips marked A″A″ and A‴ are set parallel to AA while, at the same time the members B″B″ and B‴ B‴ are set parallel to BB.

Tests have been made of the resultant states of stresses and strains produced in the trellis grips with correct and incorrect mounting of the specimens The tests were similar to those shown for the roller grips and the ordinary cloth testing machine in Figs 1(a)-(d) The experiments showed that the trellis grips in fact produced simple pulls and corresponding states of strain, if and when the specimens were correctly mounted An incorrect mounting produced in general a heterogeneous and complex state of stress and strain in the specimen with waisting and/or buckling effects If, for instance, owing to a false setting of the grips, the trellis of the grips does not coincide with that of the specimen, the theory shows that the whole area bounded by the grip contracts more quickly or less quickly than that of the specimen, and in the experiments there is shown either a buckling of the specimen to take up the surplus area, or a waisting to make good the deficiency For larger stretches, however, the heterogeneity becomes so great that in addition to the above effects new ones appear and then the specimen may show simultaneously waisting and buckling One could indeed, for not too large strains, make a first approximation to the correct mounting in a purely empirical manner by finding the position where neither buckling nor waisting occurred

Fig 5 shows side by side the result of stretching the same specimen by using angle grips under three different conditions In Fig 5(b) a simple pull has been produced with a corresponding homogeneous state of strain by a correct mounting of the specimen in the angle grips, here the trellis of the grips coincides with that of the specimen and thus neither buckling nor waisting occurs In Figs 5(a)—(c) are shown cases in which the mounting is incorrect, in the sense that the trellis of the grips does not coincide with that of the specimen, and here heterogeneous and complex states of stresses and strains appear. In Fig 5(a) the angle between the grips is too small, in Fig 5(c) too large, and corresponding waisting and buckling effects appear. [One may regard the heterogeneous states of stresses and strains obtained in the ordinary cloth testing machine (see Figs. 1(a) and 1(b)) as an extreme case of the type shown in Fig. 5(a). In fact, the two parallel clamps in the ordinary cloth testing machine can be regarded as belonging to an angle grip with a zero angle between the grips.]

A note of caution must be added at the end. When a specimen is subjected to a simple pull the corresponding state of strain will define a definite trellis of lines of zero elongation in the initial and terminal positions. If, then, the amount of the pull is varied, a corresponding variation will occur in the strain, and in general, in the trellis lines in the two positions. As the grips can be aligned in the initial position only to one definite trellis of lines of zero elongation, in principle, any setting of the trellis grips in the initial position can be correct only for one particular terminal position, and hence only for one particular amount and direction of the simple pull. It must remain a matter of experimental investigation for which samples, and with what accuracy, the same setting can be used for various amounts of pull (see next section).



(a)
Angle smaller than correct trellis angle

(b)
Correct trellis angle

(c)
Angle larger than correct trellis angle

Fig. 5

It may be noted that the use of the trellis grips is not restricted to the particular purpose discussed above. Good use can be made of these grips in all mechanical testings which aim at the imposition on a specimen of homogeneous conditions of stresses and strains in order to attain independence of the length and width of the specimen.* Two typical examples may be discussed with reference to some instruments which have been developed in the Shirley Institute for certain destructional tests under simple pull. The first instrument uses angle grips in conjunction with a Goodbrand cloth tester to determine the breaking strength of a warp- or weft-way specimen as a constant of the material independent of the dimensions of the specimen. The second instrument uses similar angle grips in conjunction with a ballistic fatigue treatment to determine, in coated fabrics, the resistance of the coating against destruction under repeated strains. Here it is convenient to use biased specimens in order to obtain, in the coating, maximum amounts of strain.

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* It is understood that the dimensions (length and width) of a specimen are varied only within regions in which sufficiently large numbers of threads are involved.

THE BEHAVIOUR OF TEXTILE FABRICS UNDER A SIMPLE PULL

We shall now discuss in some detail the behaviour of the specimens of textile fabrics at various bias angles under the action of simple pulls of various amounts.

A large number of experiments were made, first on the roller grips and then on the trellis grips. For economy of space only a representative selection of the experiments are discussed together with the corresponding photographs and tables (see Plates I to IV and Tables I to VIII) supplemented by diagrammatic schemes to illustrate the main points.

This discussion will show that the displacements of the nodal points conform to the principle of maintenance of continuity (theory of strain), *i.e.* that under simple pulls the yarns of the specimen are displaced as if they were *pinpointed* to one another at the nodal points, and that in these displacements the components of the vector of displacement vary in accordance with the *linear function* of the co-ordinates of these points. With regard to the theory of stress-strain relation we shall prove that the strained specimens exhibit the phenomena of *evading action* and *Poisson effect* predicted in the theory for anisotropic media. For ease of reference, the specimen is assumed to be taken from a woven fabric, and the threads accordingly distinguished as warp and weft, the considerations for knitted fabrics are similar except that the terms warp and weft have to be replaced by wales and courses.

(1). Pinpointing at the Nodal Points

When a specimen changes from its initial to a terminal position the threads will, in general, change their length and orientation, in addition they may either keep the point of contact at every nodal point unchanged as if they were pinpointed there, or alternatively they may glide over one another.

The experiments show that each sample fabric behaves under a simple pull, up to a certain critical value, as if the threads were pinpointed to one another at all the nodal points. It is probable that this pinpointing is due to the fact that the pull tends to press the crossing threads against one another at the nodal points and thereby increase the frictional forces by which the threads are interlocked.

There are a number of different experimental facts which provide independent evidence for the pinpointing. A mere cursory inspection of the photograph provides evidence as it is seen that the markings which were imprinted on the specimens in their initial position retain their well-defined and distinct features in all terminal positions. This evidence is best appreciated by considering that similar markings, imprinted in the initial position on a material such as a sliver, in which the fibres are not pinpointed to one another, show in the terminal positions signs of increasing disintegration and haziness with increasing amounts of pull. This was confirmed by experiments.

There is another phenomenon which strongly supports the evidence for the pinpointing. Starting with wounded specimens, in which some threads were cut deliberately at a number of points, sufficiently distant from one another, we find that under the application of simple pulls the fragments of the cut threads are displaced in a way which is indistinguishable (within the limits of the accuracy of observation) from the way in which the uncut threads are displaced. This uniformity of displacement can be readily observed with a magnifying glass and has been verified in specimens of a variety of fabrics.

A detailed inspection of the photographs provides full proof of the pinpointing. In the initial position all lines drawn on the surface of a fabric along the threads, are borne partly by the warp and partly by the weft, and photographs of these lines in the terminal positions show that although every such line breaks up into a discontinuous series of fragments* borne respectively by the warp and weft threads, all nodal points which were on a line in the initial position are on the same line in the terminal position. Since the details in the photographs are too small to be recognisable in the reproduction, schematic diagrams Figs. 6(a) to 6(c) are given instead. Fig. 6(a) corresponds to the initial position. It shows at a nodal point the intersection of a warp and weft thread, and the corresponding intersection of a pair of lines drawn on the surface of the fabric along these threads.

As the weft crosses over the warp at this nodal point it is seen that the line drawn weft-way is borne only by the weft thread, whilst the line drawn warp-way consists of three fragments, the two outer ones borne by the warp thread, and the inner one by the weft thread. For distinctness the parts of the markings borne by the warp thread are grey, whilst those borne by the weft thread are black. Fig. 6(b) corresponds to a terminal position with pinpointing at the nodal point. This pinpointing (absence of gliding) shows up in the "integrity" of the point of intersection, i.e. the fact that the same point of intersection is common to all the different fragments of the two lines. By contrast Fig. 6(c) corresponds to a terminal position for a hypothetical case with gliding at the nodal point. This gliding shows up as a disintegration in the fact that the different fragments have more than one point of intersection.

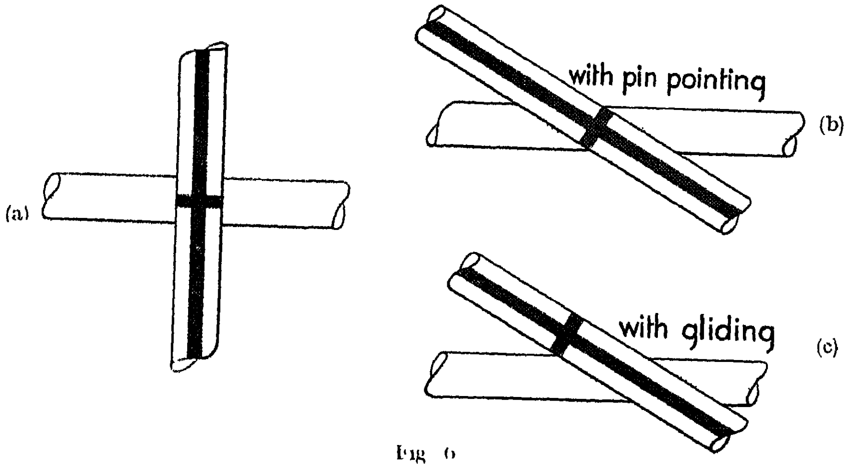

Fig. 6

In all the experiments recorded in the photographs and Tables II to VIII we found that pinpointing at the nodal points was maintained in the sense that, within the accuracy of our observations, we were unable to detect any trace of gliding, even at considerable stretches.

In order to find out the limitations of the pinpointing some bias specimens were examined in which the two grips that applied the simple pull were not attached to the same sets of threads†, and the amount of pull was increased up to the critical value at which the specimen disintegrated. The pull on the grips will then induce a tendency for the two series of threads held respectively in the upper and lower grips, to glide over one another at the nodal points, and such a gliding—if it were present—could be easily observed at the edges of the specimen where the free ends of the threads project; moreover—if gliding were present—a simple pull of ever increasing amount would ultimately disintegrate the specimen without breakage of threads, and would, in general, yield three portions, one containing the series of threads held in the upper grips, another containing similar series held in the lower grips, and a third containing the series of threads that are held in neither of the grips. A close examination of the specimens of the various samples showed that in all types of knitted and woven fabrics, including the very loosely woven fabrics (samples A, B, C and D) and the fabric with viscose rayon weft yarn (sample J) the pinpointing was maintained in general over all magnitudes of simple pulls up to the breaking point of the yarns, no trace of gliding being detectable. Gliding in the interior* can, in fact, be produced only under a combination of exceptional conditions, such as occur when specimens of fabrics of very loose weave or constructed from very slippery yarn are tested under a bias angle of about 45°; even then, pinpointing is maintained for simple pulls below some critical value (say up to 25 per cent. stretch) and only when the pull is increased above the critical value will gliding occur suddenly, and once the gliding has started the specimen will disintegrate by gliding into the three portions referred to above.

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* This break up shows that the principle of maintenance of continuity is not satisfied for the fabric as a whole, but only for its nodal points.

† In general this can be attained by choosing a bias specimen with a sufficiently high ratio of length to width.

The practical implications of the pinpointing may now be considered.

Textile fabrics suffer, under service conditions, in addition to external abrasion, pulls in various directions, and these pulls would lead to an internal wear of the fabric by abrasion of the threads through their gliding over one another, if such a gliding were not prevented through the pinpointing of the threads at their crossing points. Pinpointing thus provides a safeguard against internal abrasion and, in point of fact, the fabrics in service usually wear out under external abrasion before any sign of internal abrasion is noticeable.

Pinpointing also helps in safeguarding textile fabrics against rupture. When a fabric under load is wounded locally through some accident, say, the pinpointing of the threads at the periphery of the wound will transfer the load from the severed or weakened sets of threads to the ones not affected by the accident. The wound is thus virtually sealed off by the pinpointing, and this will restrain the tendency of the wound to spread under a load and to develop into a rupture of the fabric.

The practical importance of the pinpointing is enhanced by the fact that it persists over a large variety of different mechanical actions. However, there are conditions under which the pinpointing fails. One well illustrated example is in the slippage of threads in sleeves of garments. In some garments—particularly fairly open twill or sateen weave fabrics constructed from slippery rayon yarns—difficulty is experienced in seaming two pieces of the fabric together so as to prevent slippage of the threads through the stitched seam. This slippage may be prevented by careful attention to the construction of the stitched seam but it should be noted that the threads of the fabric are prone to slip in the body of the fabric under certain mechanical actions. For example, in the sleeve of a jacket or blouse there is a repeated bending and flexing at the elbow, and it might be expected that the local stresses at the outside of the elbow would lead to slippage of the threads of the fabric in this position. In point of fact, slippage at this point rarely occurs and is much more prevalent on the inside of the elbow. The reason for this is found in the fact that at the outside of the elbow the threads are pressed against one another under stress, and this increases the frictional forces operative at the nodal points, at the inside of the elbow the threads tend to be less firmly pressed together at a nodal point and hence slippage may occur.

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* Apart from the gliding in the interior one can observe a gliding at the exposed nodal points along the free edges of the bias specimen when the pull is raised over a certain critical value, such gliding results only in a fraying of the edges and may here be left out of the discussion since it is entirely due to the choice of non-ideal boundary conditions and may be avoided by using specimens which have no exposed nodal points, as for instance a specimen that is sewn along its free edges so as to form a tube.

Table I
Structure of Fabrics Used

Serial Letter	Fibre	Weave	Finish	Width	Weight	Threads/inch		Crimp %		Counts*		Denier	
				inches	oz /yd ²	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
A	Cotton	Square, plain	Loom state	29·6	10·8	16·9	17·5	10·1	12·7	29/4/3	29/4/3	—	—
B	Cotton	Square, plain	Loom state	27·9	4·0	11·7	11·2	4·4	3·6	11·9/3	11·7/3	—	—
C	Cotton	Rectangular, plain	Loom state	28·3	5·1	16·0	11·0	7·7	4·8	12·9/3	10·3/3	—	—
D	Cotton	Rectangular, 2/1 twill	Loom state	28·4	5·0	15·8	11·0	8·7	5·6	13·0/3	10·3/3	—	—
E	Cotton	Rectangular, poplin	Bleached, Rigmel shrunk	39·5	3·2	150	75	8·7	4·0	106/2	105/2	—	—
F	Cotton	Rib knitted	Loom state	(circular)	6·6	51 (wales)	44 (courses)	—	—	26·1	26·1	—	—
G	Wool	Rectangular, plain	—	31·8	5·9	48	30	10·1	1·6	23/2	17/2	—	—
H	Silk	Square, plain . .	Degummed	36·2	1·5	116	113	7·2	3·9	—	—	20/22 3 thread	20/22 3 thread
I	Nylon	Square, plain	—	36·2	1·6	127	119	3·9	6·5	—	—	49	48
J	Viscose rayon	Rectangular, plain	—	35·1	2·6	72	53	1·2	7·9	—	—	150	164
K	Acetate/viscose rayon	Rectangular, crepe satin	Dyed	24·1	7·3	365	61	13·0	60	—	—	76	259

* Expressed in cotton 840 yd hank system

Table III
Trellis of Bias Specimens of Fabric (A) (Roller Grip Experiments)

Specimen In Initial Position		Simple Pull to Stretched Length	Specimen in Successive Terminal Positions										Trellis Calculated for Initial Position	
Material	Nominal bias angle		Structure				Deformation				Trellis			
			Warp		Weft		Major axis		Minor axis		Lines of zero elongation		Opening angle ϵ_o degrees	Evasion angle χ_o degrees
			Length	Orientation degrees	Length	Orientation degrees	Length	Orientation degrees	Length	Orientation degrees	Orientation degrees	Orientation degrees		
Fabric A. Loom-state cotton fabric " Square " plain weave with cabled yarns	0°	100·0	100·0	0	100·0	90	100·0	—	100·0	—	—	—	—	—
		107·4	107·4	0	95·6	90	107·4	0	95·6	−90	−50	50	53·3 } 51·8	0·0 } 0·0
		114·1	114·1	0	88·9	90	114·1	0	88·9	−90	−43	43	50·2	0·0
	−11°	100·0	100·0	−13½	100·0	76½	100·0	—	100·0	—	—	—	—	—
		108·1	104·4	−12½	97·8	67½	111·1	19½	88·9	−70½	−24½	61	49·1	23·9
		117·0	108·9	−10	95·6	56½	122·3	15½	76·3	−74½	−20	50	48·3 } 48·9	23·9 } 24·1
		120·0	111·1	− 9	94·8	51	126·7	13½	68·9	−76½	−18½	45½	49·0	23·8
		127·4	114·8	− 8	94·8	41½	135·6	11½	59·3	−78½	−16	37½	49·0	24·9
	−22½°	100·0	100·0	−26½	100·0	63½	100·0	—	100·0	—	—	—	—	—
		110·4	100·7	−23½	98·5	55½	112·6	15	87·0	−75	−23½	54½	46·3	19·2
		117·0	103·0	−21	97·8	50	119·3	12	79·2	−78	−24½	46½	47·0 } 48·2	17·3
		125·2	104·4	−17½	97·0	42½	128·8	9½	68·9	−80½	−22½	39½	48·3	17·3 } 18·1
		131·9	107·4	−14½	97·0	35	136·3	8	59·3	−82	−19	34	48·9	17·9
		138·5	110·4	−12	98·5	28½	144·5	7	49·6	−83	−17	28½	50·7	18·9
	−45°	100·0	100·0	−45	100·0	43½	100·0	—	100·0	—	—	—	—	—
		111·1	100·0	−40	100·0	38½	111·1	− ½	89·6	89½	−41	39½	46·4	−0·6
		118·5	100·0	−35	100·0	36	118·5	0	80·7	90	−37	35½	47·1 } 47·8	0·0
		127·4	100·0	−29½	100·0	30½	127·4	0	69·6	90	−30	30	46·6	0·0 } −1·0
		136·3	99·3	−24½	100·7	24½	136·3	− 1	59·3	89	−27½	26½	49·5	−2·0
		142·2	100·0	−19½	100·0	20½	142·6	− 1	51·1	89	−23½	22	49·4	−2·4
	−67½°	100·0	100·0	−68	100·0	22½	100·0	—	100·0	—	—	—	—	—
		110·3	98·5	−59½	101·5	20	112·5	−14½	88·3	75½	−53	27	46·8	−18·1
		114·7	97·8	−53½	103·0	18	117·6	−13	80·9	77	−49	23	46·6 } 47·9	−18·8
		126·5	97·8	−43	108·1	14½	130·2	−10	66·2	80	−39	18½	47·2	−19·6 } −18·9
		131·6	97·1	−38	110·3	12½	136·0	− 8½	58·8	81½	−35	18	49·1	−18·8
		136·0	100·0	−32	112·5	10½	143·4	− 7	50·7	83	−30	15½	49·8	−19·4
	−79°	100·0	100·0	−77½	100·0	12½	100·0	—	100·0	—	—	—	—	—
		107·4	96·3	−70	103·7	11	109·6	−18	88·9	72	−57½	22½	46·0	−21·7
		117·0	93·3	−60½	109·6	9½	120·0	−14	77·0	76	−48½	19½	46·4 } 46·9	−21·6 } −22·4
		122·2	92·6	−52½	112·6	8½	126·6	−13	68·9	77	−43½	18	47·4	−23·4
		125·2	92·6	−46½	114·8	7½	131·1	−11½	63·0	78½	−40½	15½	47·9	−23·0
	−90°	100·0	100·0	−90	100·0	0	100·0	—	100·0	—	—	—	—	—
		108·2	92·6	−90	108·2	0	108·2	0	92·6	90	−43	43	47·5 } 47·4	0·0 } 0·0
		112·6	87·4	−90	112·6	0	112·6	0	87·4	90	−40	40	47·3	0·0

Table IV
Trellis of 22½° Bias Specimens of Various Fabrics (Roller Grip Experiments)

Specimen in Initial Position		Simple Pull to Stretched Length	Specimen in Successive Terminal Positions										Trellis Calculated for Initial Position	
			Structure				Deformation				Trellis			
			Warp		Weft		Major axis		Minor axis		Lines of zero elongation			
Material	Nominal bias angle		Length	Orientation degrees	Length	Orientation degrees	Length	Orientation degrees	Length	Orientation degrees	Orientation degrees	Orientation degrees	Opening angle ϵ_0 degrees	Evasion angle χ_0 degrees
Fabric A. Square, plain, loom state, cotton fabric	−22½°	100.0	100.0	−26½	100.0	63½	100.0	—	100.0	—	—	—	—	—
		110.4	100.7	−23½	98.5	55½	112.6	15	87.0	−75	−23½	54½	46½	19
		117.0	103.0	−21	97.8	50	119.3	12	79.2	−78	−24½	46½	47	17½
		125.2	104.4	−17½	97.0	42½	128.8	9½	68.9	−80½	−22½	39½	48½ }48	17½ }18
		131.9	107.4	−14½	97.0	35	136.3	8	59.3	−82	−19	34	49	18
		138.5	110.4	−12	98.5	28½	144.5	6	49.6	−83	−17	28½	50½	17
Fabric B. Square, plain, loom state, cotton fabric	−22½°	100.0	100.0	—	100.0	—	100.0	—	100.0	—	—	—	—	—
		106.3	102.1	−20½	100.0	62	107.7	19	93.7	−71	−25	64	48½	22
		112.7	102.8	−19	100.0	52	116.1	16	82.4	−74	−23½	54	48½	22½
		119.0	104.2	−15½	100.0	43	125.3	13	69.0	−77	−18	43	47 }48	22½ }22
		123.9	104.2	−13	99.3	35½	130.3	10	58.4	−80	−16	35	47	22
		126.8	104.9	−11½	99.3	30	133.8	8½	49.3	−81½	−15	29	47½	22
		132.4	106.3	−9	99.3	22½	138.3	6	37.3	−84	−11	22½	48	20½
Fabric C Rectangular, plain, loom state, cotton fabric	−22½°	100.0	100.0	—	100.0	—	100.0	—	100.0	—	—	—	—	—
		106.3	100.7	−24½	100.7	57½	107.7	16	93.7	−74	−26½	55½	45	18
		112.7	100.7	−22	100.0	51½	114.0	15	83.8	−75	−24½	53½	48	19½
		121.1	102.1	−19	100.0	41½	124.0	10	70.4	−80	−22½	43	48½ }47	17½ }19
		126.1	103.5	−16	100.0	36	129.6	10	62.0	−80	−17½	38	47½	20
		128.9	105.6	−13½	100.0	30½	135.2	8	52.8	−81	−15	30	46½	19½
		136.6	107.7	−9½	100.0	22½	141.6	5½	38.7	−81	−11	22	47½	19½
Fabric D. Rectangular, 2/1 twill, loom state, cotton fabric	−22½°	100.0	100.0	—	100.0	—	100.0	—	100.0	—	—	—	—	—
		108.4	100.0	−22½	100.7	54½	112.7	15½	88.0	−74½	−21	55	45	19½
		115.5	102.1	−20½	99.3	49	117.6	12	91.0	−78	−22½	46½	45	17
		122.5	103.5	−16½	100.7	39½	126.8	10½	66.9	−79½	−18	39	46 }46	19½ }19
		129.6	104.2	−13	100.0	33	132.3	9	54.2	−81	−14	32	46	21
		133.1	105.6	−10½	100.0	28½	136.7	6½	46.4	−83½	−12½	27½	47	18½
		136.6	105.6	−8½	101.4	22	140.9	5	38.7	−85	−11	21½	46½	17½
		142.3	107.0	−5½	102.8	15½	147.2	3½	26.8	−86½	−6½	15	46	18½
Fabric E. Rectangular, bleached poplin, cotton fabric	−22½°	100.0	100.0	−22½	100.0	66½	100.0	-	100.0	—	—	-	—	—
		108.7	101.3	−21	100.0	58½	110.0	16½	90.0	−73½	−25½	57½	47½	20
		116.0	104.0	−19½	100.0	52½	118.0	15	81.3	−75	−23½	53	49 }49	21 }20½
		125.3	106.7	−15½	101.3	41½	130.0	11½	68.6	−78½	−21½	43	50	21
		127.3	107.3	−14½	100.0	38	133.3	10	62.7	−80	−20	40	51	20½

Table IV—*continued*

Specimen in Initial Position		Simple Pull to Stretched Length	Specimen in Successive Terminal Positions										Trellis Calculated for Initial Position			
			Structure				Deformation				Trellis					
			Warp		Weft		Major axis		Minor axis		Lines of zero elongation		Opening angle ϵ_0		Evasion angle χ	
Material	Nominal bias angle		Length	Orientation	Length	Orientation	Length	Orientation	Length	Orientation	Orientation	Orientation				
Fabric F. Loom state rib knitting	−22½°	100·0	100·0	−20½	100·0	67½	100·0	—	100·0	—	—	—	—	51	—	10
		113·0	107·0	−17½	95·7	60	111·3	6	88·7	−84	−38	48	49½		7	
		127·0	117·4	−13½	93·9	47½	126·2	7	72·2	−83	−29	41	50½		12	
		137·4	124·3	−11	90·4	41	137·0	5	61·8	−85	−24½	32½	50½		11	
		149·6	134·8	−8	89·6	31	148·7	4	48·7	−86	−20	26	52½		11½	
		161·7	143·5	−6	91·3	24	161·7	2	39·1	−88	−16½	19½	53½		8½	
Fabric G Rectangular, plain, woollen fabric	−22½°	100·0	100·0	−23½	100·0	66½	100·0	—	100·0	—	—	—	—	45	—	21½
		101·9	100·6	−22	100·0	65½	102·6	20	98·2	−70	−22½	60½	43		21	
		106·8	100·0	−20½	99·4	58	110·0	20	89·6	−70	−18½	59	44½		24	
		114·3	100·6	−17½	100·0	49	119·3	14½	77·7	−75½	−17½	47½	44½		21½	
		121·1	101·2	−15	99·4	40½	126·2	12	66·6	−78	−16	39½	45		22½	
		123·6	104·3	−13	98·1	36½	130·0	9½	60·3	−80½	−16	35	46		20	
		128·6	106·8	−11½	98·1	33½	134·3	9	54·7	−81	−15	32	47		20½	
Fabric H. Square, plain, degummed silk fabric	−22½°	100·0	100·0	—	100·0	—	100·0	—	100·0	—	—	—	—	48	—	19½
		105·6	100·7	−22	100·7	59½	106·2	19	95·1	−71	−28	64	49		21	
		113·2	101·4	−19½	100·0	51½	115·9	15½	83·3	−74½	−23	54	48		21	
		120·8	104·2	−16½	99·3	42	126·3	11	68·7	−79	−20	42	48		20	
		126·4	106·3	−14	99·3	36½	131·9	9	59·7	−81	−18	35½	48		18½	
		131·2	109·0	−12	97·9	31½	136·1	7	53·5	−83	−16	30½	47½		17½	
Fabric I. Square, plain nylon fabric	−22½°	100·0	100·0	−22½	100·0	67½	100·0	—	100·0	—	—	—	—	46½	—	22½
		108·2	100·0	−20½	100·0	59½	110·0	19	88·2	−71	−21	59	46½		23	
		113·5	100·0	−18½	100·0	48½	118·2	14½	76·5	−75½	−19	48½	46		22	
		118·8	101·8	−16	100·0	42	124·1	12½	67·7	−77½	−18	42	46½		22	
Fabric J. Rectangular, plain, viscose rayon, finished fabric	−22½°	100·0	100·0	−22½	100·0	67½	100·0	—	100·0	—	—	—	—	44	—	22
		105·3	100·0	−20	100·0	61	107·3	19	91·5	−71	−20	59	44		22	
		110·4	100·7	−19	98·7	52	114·5	16	80·9	−74	−17	50	43		22	
		116·4	100·7	−16	98·7	46	122·4	14½	71·1	−75½	−16	44	45		24	
		121·7	101·3	−17	100·0	35	128·9	9½	59·9	−80½	−14	35	44½		20	
Fabric K. Rectangular, crepe satin, dyed acetate/viscose rayon	−22½	100·0	100·0	—	100·0	—	100·0	—	100·0	—	—	—	—	51½	—	27½
		105·9	100·6	−17½	100·0	59½	109·4	19	90·0	−71	−21½	59½	46		22½	
		111·8	101·8	−15½	102·9	51½	118·3	17	83·5	−73	−21½	54½	48		23	
		118·8	103·5	−15	107·6	46	127·9	16½	77·7	−73½	−18½	52	49½		26	
		128·8	105·9	−14	119·4	38	143·0	15	69·4	−75	−16	47½	52		29	
		137·6	107·1	−11½	131·8	29	157·7	12½	60·6	−77½	−16	42	55½		30	
		146·5	109·4	−10	146·5	23	173·6	11½	51·8	−78½	−13½	36½	57½		34	

Table V
Trellis of Various Bias Specimens of Fabric (F) (Roller Grip Experiments)

Specimen in Initial Position		Simple Pull to Stretched Length	Specimen in Successive Terminal Positions										Trellis Calculated for Initial Position	
			Structure				Deformation				Trellis			
			Wales		Courses		Major axis		Minor axis		Lines of zero elongation			
Material	Nominal bias angle		Length	Orientation degrees	Length	Orientation degrees	Length	Orientation degrees	Length	Orientation degrees	Orientation degrees	Orientation degrees	Opening angle ϵ_0 degrees	Evasion angle χ_0 degrees
Fabric F. Loom state circular rib knitting	0°	100·0	100·0	0	100·0	90	100·0	—	100·0	—	—	—	—	—
		114·7	114·8	0	87·8	91½	114·7	−1½	87·8	−91½	−45	41½	51	−2
		126·2	126·1	0	77·4	93	126·2	−1½	77·4	−91½	−36½	33½	49	−2½
		138·3	138·3	0	65·2	92½	138·3	−½	65·3	−90½	−30	29	50 } 51½	−1 } −1
		148·7	148·7	0	57·4	92	148·7	0	57·4	−90	−27	27	53	0
		163·5	163·5	0	48·7	92	163·5	0	47·9	−90	−23	23	55½	0
	−11°	100·0	100·0	−11½	100·0	76½	100·0	—	100·0	—	—	—	—	—
		114·8	113·0	−8½	88·7	69½	113·9	1	86·1	−89	−38	41	47½	1½
		125·2	122·6	−6½	80·9	62½	124·4	3	72·2	−87	−30½	35½	48	5½
		137·4	134·8	−5½	70·5	53½	137·4	2	58·3	−88	−24	27	48½ } 49½	5½ } 4
		149·6	147·0	−3½	62·6	45½	148·7	1	46·1	−89	−20½	23	52	4
		160·0	156·5	−3	60·9	39	159·2	1	40·0	−89	−17½	18½	52	3
	−22½°	100·0	100·0	−20½	100·0	67½	100·0	—	100·0	—	—	—	—	—
		111·3	107·0	−17½	95·7	60	111·3	6	88·7	−84	−38	48	49½	7
		127·0	117·4	−13½	93·9	47½	126·2	7	72·2	−83	−29	41	50½	12
		137·4	124·3	−11	90·4	41	137·0	5	61·8	−85	−24½	32½	50½ } 51	11 } 10
		149·6	134·8	−8	89·6	31	148·7	4	48·7	−86	−20	26	52½	11½
		161·7	143·5	−6	91·3	24	161·7	2	39·1	−88	−16½	19½	53½	8½
	−45°	100·0	100·0	−44	100·0	42	100·0	—	100·0	—	—	—	—	—
		113·9	100·9	−40	104·3	38	113·9	6½	92·2	−83½	−43½	55½	55½	8
		123·5	100·0	−37	113·0	32½	124·3	7½	86·9	−82½	−40	54	57	10½
		139·1	99·1	−32½	124·3	26	139·1	9½	78·3	−80½	−31½	49½	56½	16½
		151·3	98·3	−29	136·5	21	152·1	8½	69·6	−81½	−27½	42½	57 } 57	18 } 15½
		161·7	97·4	−26½	145·2	17½	163·5	6	63·0	−84	−25	38½	58	15
		175·7	95·7	−24½	162·6	13½	180·9	6½	53·0	−83½	−19½	31½	58½	21
		186·1	94·8	−21	177·4	11	194·0	5	47·0	−85	−17	29	60½	20

Table V—*continued*

Specimen in Initial Position		Simple Pull to Stretched Length	Specimen in Successive Terminal Positions										Trellis Calculated for Initial Position			
			Structure				Deformation				Trellis					
Material	Nominal bias angle		Wales		Courses		Major axis		Minor axis		Lines of zero elongation		Opening angle ϵ_0		Evasion angle χ_0	
			Length	Orientation	Length	Orientation	Length	Orientation	Length	Orientation	Orientation	Orientation				
Fabric F. Loom state circular rib knitting	−67½°	100.0	100.0	−68	100.0	22	100.0	—	100.0	—	—	—	—	64	—	7
		111.3	98.3	−64½	109.6	18½	111.3	0	94.8	−90	−55½	56½	61		0	
		123.5	95.7	−62½	120.0	17½	123.9	3	91.3	−87	−52½	58½	63		4	
		135.7	93.0	−62½	132.2	16½	135.6	3	87.0	−87	−48½	53½	62½		4½	
		149.6	91.3	−58	146.1	12½	149.5	3	82.6	−87	−44	50	62½		5½	
		161.7	87.8	−55½	156.5	10½	162.6	3½	76.5	−86½	−40	47	63½		7½	
		175.7	82.6	−51	170.4	9	175.6	1½	70.4	−88½	−36	41	63		3½	
		190.4	79.1	−49½	185.2	6½	190.4	3½	64.3	−86½	−32½	37½	64		10	
		203.5	74.8	−46½	200.0	5½	204.3	3	58.3	−87	−29	34	65		10½	
		217.4	71.3	−46	214.8	5	219.1	3	53.9	−87	−25½	31	65½		12	
		225.2	67.8	−44½	224.3	4½	228.7	2½	50.4	−87½	−25	29	66½		11	
		238.3	64.3	−43½	239.1	3	243.4	2	47.0	−88	−23	27	67½		10	
	−79°	100.0	100.0	−80	100.0	10	100.0	—	100.0	—	—	—	—	66	—	1
		111.2	96.5	−80½	110.4	7½	111.2	0	96.5	−90	−55	56	59		0	
		126.0	93.9	−77	125.2	7	126.0	0	93.9	−90	−57½	58½	65		0	
		138.1	91.3	−76	136.5	6	138.1	0	89.6	−90	−55	56	66		0	
		152.1	87.0	−74½	151.3	5½	152.1	0	85.2	−90	−51	52	66		0	
		165.1	82.6	−73½	164.3	4	165.1	0	82.6	−90	−48	48	66		0	
		175.7	80.0	−71	173.9	4	175.7	0	78.3	−90	−44½	45½	66		0	
		186.8	75.7	−69½	187.0	3½	186.8	0	73.9	−90	−40	42	65½		0	
		200.0	73.0	−68	200.0	3	199.9	1½	69.6	−88½	−38	40	66½		4½	
		214.8	67.8	−67½	213.9	2½	214.7	1	64.4	−89	−35	37	67½		3½	
		224.3	63.5	−66½	223.5	2½	224.3	0	60.9	−90	−32½	33½	67½		0	
		236.5	59.1	−64½	237.4	2½	236.5	−½	54.8	−90½	−31	31	69		2	
		247.9	54.8	−64½	246.1	2½	247.9	½	52.2	−90	−28	29½	69		2½	
	−90°	100.0	100.0	−90	100.0	0	100.0	—	100.0	—	—	—	—	67½	—	−1
		115.6	97.4	−90	115.7	0	115.6	−½	97.4	−90½	−63½	62½	67		−½	
		127.8	93.9	−90	127.8	0	128.7	−3	93.9	−93	−61	56	66		−4	
		140.0	91.3	−90	140.0	0	140.9	−2	90.5	−92	−56½	54½	66		−3	
		154.8	87.0	−90	154.8	0	154.8	0	87.0	−90	−53½	53½	67½		0	
		165.2	82.6	−90	165.2	0	166.1	0	82.6	−90	−49	49	66½		0	
		176.5	80.0	−90	176.5	0	176.5	−1	80.0	−91	−47½	47	67½		−2	
		189.6	75.7	−90	189.6	0	189.6	0	75.7	−92	−45	44	68		0	
		205.2	70.4	−90	205.2	0	205.2	0	70.5	−90	−40	40	67½		0	
		215.7	67.0	−90	215.7	0	215.7	0	67.0	−90	−37½	38½	68		0	
		225.3	64.3	−90	225.2	0	225.3	0	64.4	−90	−36½	35	68½		0	
		244.4	57.4	−90	244.3	0	244.4	−1	57.4	−91	−33½	32½	70		−4	

Table VI
Trellis of 22½° Bias Specimens of Various Fabrics (Angle Grip Experiments)

Specimen in Initial Position		Simple Pull to Stretched Length	Specimen in Successive Terminal Positions										Trellis Calculated for Initial Position			
			Structure				Deformation				Trellis					
			Warp		Weft		Major axis		Minor axis		Lines of zero elongation					
Material	Nominal bias angle		Length	Orientation degrees	Length	Orientation degrees	Length	Orientation degrees	Length	Orientation degrees	Orientation degrees	Orientation degrees	Opening angle ϵ_o degrees		Evasion angle χ_o degrees	
Fabric A. Square, plain, loom state, cotton fabric	−22½°	100.0 106.7 114.0 118.7 126.7 131.3	100.0 100.7 104.0 104.7 108.0 110.0	−22½ −20 −17½ −15½ −12½ −10½	100.0 98.7 98.7 98.7 99.3 99.3	68 60½ 51 45 35½ 26½	100.0 108.6 118.0 123.3 133.3 138.0	— 14½ 12½ 10 8 6	100.0 90.7 81.3 72.7 60.0 48.7	— −75½ −77½ −80 −82 −84	— −26 −22 −22 −17½ −15	— 56 48 41 33 26	— 46 45½ 46 46½ 46½	46	— 17 18 16½ 18 16½	17
Fabric B. Square plain, loom state, cotton fabric	−22½°	100.0 107.4 112.0 116.0 121.3 126.7	100.0 99.3 101.3 100.7 102.0 104.7	−22½ −18 −15 −14 −12 −10	100.0 100.7 100.0 100.0 101.3 102.0	67½ 59 53 46 37 29	100.0 110.0 116.0 122.7 131.3 136.8	— 21 18 16 11 8	100.0 88.7 82.0 73.3 60.7 48.0	— −69 −72 −74 −79 −82½	— −19½ −18 −16½ −14½ −12½	— 60 54 47 36½ 28	— 46 46 46 46 46½	46	— 25½ 24½ 25½ 23 22	24
Fabric C. Rectangular, plain, loom state, cotton fabric	−22½°	100.0 107.4 115.3 118.7 123.3 130.0	100.0 101.3 101.3 101.3 103.3 105.3	−22½ −19 −17 −14 −12 − 9	100.0 102.7 102.7 102.0 102.7 102.7	67½ 63 50 45 38 30	100.0 108.8 119.2 125.2 130.8 137.2	— 22 18 15½ 12½ 9½	100.0 94.0 81.3 72.7 64.6 50.0	— −68 −72 −74½ −77½ −80½	— −21½ −19 −16 −15 −13½	— 67½ 55½ 47½ 39 29	— 49 48 47 46 47	47½	— 25 25½ 25½ 24 24½	25
Fabric D Rectangular, 2/1 twill, loom state, cotton fabric	−22½°	100.0 108.6 115.9 120.5 126.5 132.5	100.0 101.3 102.0 103.3 106.0 106.6	−22½ −20½ −19 −16 −13 −10	100.0 100.0 100.0 100.7 100.7 98.7	67½ 60 51½ 43 36 27	100.0 112.5 117.8 124.4 132.3 138.2	— 17 13 12½ 10 7	100.0 91.9 81.3 72.9 58.8 44.3	— −73 −77 −77½ −80 −83	— −23½ −21 −19 −16 −12½	— 58 48½ 42 34 24	— 46½ 45 45 46½ 46	46	— 20 18½ 21 21½ 21	20½
Fabric F Loom state, rib knitting	−22½°	100.0 112.8 124.6 138.4	100.0 107.2 114.4 122.9	−22½ −18½ −14½ −10	100.0 98.0 96.1 94.8	64 53 45 34½	100.0 113.1 125.9 140.3	— 8 6 5	100.0 87.8 75.4 58.4	— −83 −84 −85	— −35 −29 −23	— 50½ 40 32	— 50 49 51½	50	— 10 10½ 11½	10½
Fabric G. Rectangular, plain, woollen fabric	−22½°	100.0 106.0 111.3 116.7 120.7	100.0 100.0 100.0 100.0 100.0	−22½ −20½ −19 −16 −13½	100.0 100.0 100.0 100.0 100.0	67 60 52 45½ 37	100.0 108.6 116.1 123.3 128.0	— 20 16½ 13½ 11	100.0 92.0 83.4 70.7 59.4	— −70 −73½ −76½ −79	— −20 −19 −17½ −13½	— 60 52 45½ 37	— 44½ 45 47 45½	45½	— 23½ 22½ 22½ 22½	22½
Fabric I Square, plain, nylon fabric	−22½°	100.0 107.3 112.0 117.3 119.3	100.0 100.0 100.0 100.0 100.0	−22½ −20½ −18 −16 −14	100.0 100.0 100.0 100.0 100.0	66½ 59 52 43½ 36½	100.0 108.6 116.1 122.7 126.7	— 18 16 13½ 10½	100.0 92.0 82.7 70.7 59.3	— −72 −74 −76½ −79½	— −20½ −18 −16 −14	— 59 52 43½ 36½	— 44½ 44½ 45 45	45	— 21 21½ 21 21½	21½

Table VII

Trellis of 22½° Bias Specimens of Various Fabrics (Parallelogram Grip Experiments)

Specimen in Initial Position		Simple Pull to Stretched Length	Specimen in Successive Terminal Positions										Trellis Calculated for Initial Position			
			Structure				Deformation				Trellis					
			Warp		Weft		Major axis		Minor axis		Lines of zero elongation		Opening angle ϵ_o Degrees		Evasion angle χ_o Degrees	
Material	Nominal bias angle		Length	Orientation degrees	Length	Orientation degrees	Length	Orientation degrees	Length	Orientation degrees	Orientation degrees	Orientation degrees				
Fabric E. Rectangular, bleached poplin, cotton fabric	−22½°	100.0	100.0	−21½	100.0	66½	100.0	—	100.0	—	—	—	—	50	—	20½
		107.3	101.3	−19½	100.0	59½	108.6	17½	91.4	−72½	−26½	63	49½		20½	
		113.2	104.6	−18	100.0	53	117.2	15	83.4	−75	−24½	56	50		20½	
		119.9	104.6	−15½	99.3	45	124.5	12½	74.2	−77½	−22½	47½	49½		20½	
		127.2	106.6	−13½	100.7	35½	134.4	9½	61.6	−80½	−20½	37	50		20	
Fabric H. Square, plain, degummed silk fabric	−22½°	100.0	100.0	−21	100.0	70½	100.0	—	100.0	—	—	—	—	46½	—	24
		106.7	100.7	−18	100.0	54	111.3	21½	92.0	−68½	−21	63	47½		25½	
		110.7	101.3	−16	98.7	52	114.7	17	80.0	−73	−19½	54	47		23½	
		116.0	102.0	−14	92.0	43	121.3	12	63.3	−78	−16½	39½	45½		22	
Fabric J. Rectangular, plain, viscose rayon finished fabric	−22½°	100.0	100.0	−23½	100.0	66½	100.0	—	100.0	—	—	—	—	44	—	20½
		102.6	99.3	−21½	98.0	60	106.1	18	89.9	−72	−20	57	43		21	
		109.2	99.3	−18½	97.3	50	116.2	14	77.8	−76	−18	46½	43½		20½	
		112.5	100.7	−17½	96.6	42½	120.2	12	68.5	−78	−17	39½	43½		20½	
		118.4	100.7	−15	97.3	35½	126.8	10	59.7	−80	−14½	35½	44½		20½	
		123.7	101.3	−13	100.0	30½	134.2	8	51.7	−82	−13	29	45		20	
Fabric K. Rectangular, crepe satin, dyed acetate/viscose rayon	−22½°	100.0	100.0	−22½	100.0	67½	100.0	—	100.0	—	—	—	—	52½	—	26½
		110.1	102.7	−19	102.0	57½	112.0	19	90.0	−71	−22	59½	47		23½	
		115.4	104.0	−17	104.7	50½	120.0	18	84.7	−72	−22½	58	50		25	
		124.2	107.3	−16	116.0	43	133.3	17	78.0	−74	−23	56½	55		27½	
		132.9	110.7	−12	123.3	36	144.0	15	70.0	−76½	−20	49	54½		29	
		140.3	114.0	−12	128.0	29	154.0	11	54.7	−80	−17	38	56		28½	

Table VIII
Collected Values of Trellis for Initial Position (—22½° Bias Angle)

Serial letter	Roller grips		Trellis grips			
			Angle		Parallelogram	
Fabric	Opening angle ϵ_o degrees	Evasion angle χ_o degrees	Opening angle ϵ_o degrees	Evasion angle χ_o degrees	Opening angle ϵ_o degrees	Evasion angle χ_o degrees
A	48	18	46	17	—	—
B	48	22	46	24	—	—
C	47	19	47½	25	—	—
D	46	19	46	21	—	—
E	49	20½	—	—	50	20½
F	51	10	50	10½	—	—
G	45	21½	45½	22½	—	—
H	48	19½	—	—	46½	24
I	46½	22½	45	21½	—	—
J	44	22	—	—	44	20½
K	51½	27½	—	—	52½	26½

(2) Linearity

It has already been shown in the previous section that a homogeneous state of strain is produced by a simple pull. All experiments in the roller and trellis grips have confirmed this as was shown with reference to Figs 1(c) and 1(d) Further evidence to the same effect is seen in the photographs from the fact that the circle drawn in the initial position becomes an ellipse in the terminal position This is proved in a quantitative way by the data given in Table II where the experimental measurements are compared with the theoretical values. Departure from linearity, however, may occur in heavily starched or filled textile fabrics. As evidence of this a bias specimen of filled scrim fabric, actually a heavily starched "anti-scatter" netting for the protection of windows, was marked with a circle and stretched between roller grips in the usual manner In this case the circle changed into a "distorted ellipse" with a very jagged boundary, the distortion being due to an irregular failure of the cementing film under the swivelling of the threads.

(3) Evading Action and Poisson Effect

When a specimen of fabric is subjected to a series of simple pulls of increasing amounts its behaviour may be observed by a study of the changes in the markings imprinted on the fabric

Plates I and II illustrate the behaviour of the sample fabrics (A) and (F), respectively, specimens of which have been subjected in the roller grips to simple pulls in various directions and to various amounts The photographs are in seven rows, corresponding respectively to seven specimens, cut out at bias angles of 0°, −11°, −22½°, −45°, −67½°, −79°, and −90° In each row the direction of the pull is kept constant and the amount is steadily increased from left to right

Plate III shows in a similar manner the behaviour of the different kinds of fabric, (A) to (G), in specimens that are all cut out at the same bias angle of −22½° and stretched in roller grips by gradually increasing amounts of pull

Plate IV finally shows the behaviour of some of the same set of fabrics for specimens that are also cut out at bias angles of −22½° but stretched in angle or parallelogram grips

The photographs, reproduced in Plates I-IV, show the patterns of markings in the initial and terminal positions These patterns imply a complete characterisation of the stresses and strains involved and in order to appreciate the implications we shall make the characterisation explicit

The stress and the strain can be characterised in the terminal position by the directions and values of their main axes For the stress, in this case the simple pull, one main axis, termed major, has a value equal to the amount of pull per unit width of the specimen in the terminal position, and has a direction extending lengthwise in the specimen, along the central marked line. The other main axis, termed minor, has always zero value, and extends perpendicular to the direction of the pull, that is widthwise in the specimen, and at right angles to the marked central line For the strain the main axes coincide in values and directions with those of the strain ellipse In general, these axes rotate from the initial to the terminal position by an angle referred to as the *angle of rotation*

Woven and knitted textile fabrics are anisotropic materials For these the relationships between the stresses and strains allow the directions of their main axes to deviate from one another, the deviation depending on the bias angle under which the simple pull is applied In the general case, that is for a simple pull at an arbitrarily chosen bias angle, the directions of the main axes of the stress differ from those of the strain and the specimen appears to execute an *evading* action since the maximum elongation occurs in a direction which is at an angle to that of the pull The *angle of evasion* is defined as the angle between the major axes of stress and strain, i.e between the direction of pull and the major axis of the strain ellipse The strain here is compounded of a pure strain, extending its main axes at finite angles to the length and "width" direction, and a rotation which turns the specimen round and brings the direction of maximum elongation nearer to that of the pull. In special cases, that is for a set of specially selected bias angles, the deviation between the directions of the main axes of stress and strain will be zero in the initial position, and then the specimen will suffer a strain which is a pure one, free from evasion and rotation.

In addition to the deviation in the directions there is for the stress and strain a disparity in their main values, as for the strain both values are finite, while for the stress, one is finite and the other zero This gives rise to a *Poisson effect,* that is to an elongation lengthwise combined with a contraction widthwise

In the experiments with the endless belt specimens on roller grips, the Poisson effects with and without evading action show up rather strikingly in the behaviour of the specimen In the experiments with the trellis grips the effect is less striking, because the evading action and the Poisson effects have been anticipated in the location and movement of the grips so that relative motion between them and the material is eliminated

Plate III shows photographs of roller grip experiments for a variety of sample fabrics, (A) to (G), where the direction of pull is chosen arbitrarily, at a nominal bias angle of $-22\frac{1}{2}°$ The belt here suffers a compounded strain extending lengthwise and contracting widthwise in accordance with the Poisson effect, and evading the direct action of the pull, as a circle drawn on the fabric extends into an ellipse in a direction different from that of the pull In this evading action, the belt is seen to suffer a pure strain with maximum elongations and contractions occurring in directions oblique to the length and width directions of the specimen, and to suffer, in addition, a rotation which carries parts of the specimen over the rollers, in spite of the strong frictional forces present, one free edge of the front sheet of the belt moving upwards over the rollers, and the other free edge of this sheet moving downwards The movement over the rollers can most readily be observed by putting the seam of the belt near to the rollers in the initial position Plate IV shows photographs of a similar series of experiments carried out in trellis grips.

When the direction of the pull is systematically varied over the full circle of directions for the same fabric, the variation of the Poisson effect and of the evading action with the change in the direction of the pull can be seen. In this way it is possible to determine the directions along which a pull produces a pure strain with no evading action, and a Poisson effect in which the maximum changes in length occur lengthwise and widthwise in the specimen

The presence or absence of an evading action is related to the precise character of the anisotropy of the material, in this case to the change over a full circle of directions, of the extensibility of the fabric under the action of a simple pull For a continuous change of the bias angle, the extensibility along the direction of pull varies continuously and assumes extreme values, alternately maxima and minima, in certain special directions The complete set of such special directions will always include the directions of symmetry, in this case the two yarn directions in the fabric, since along a direction of symmetry every property of the fabric must assume an extreme value compared with neighbouring directions For woven fabrics the extreme values along both yarn directions are minima, and one must therefore expect that in every quadrant bounded by the yarn directions the extensibility in changing from one minimum value to the other must pass through at least one other extreme value, a maximum In fact, in the quadrant of bias angles investigated, the experiments show the existence of such a maximum in directions near to the bisectrices of the warp and weft with bias angles approximately ±45°. This distribution of the maxima and minima is characteristic of all the woven fabrics Plate I shows for a typical example (sample A) the results of experiments in a systematic series of bias angles of nominal values 0°, −11°, −22½°, −45°, −67½°, −79°, and −90° A compounded strain, with an evading action and Poisson effect is seen at all bias angles except at 0°, −45° and −90°, corresponding to the set of special directions of pull for which the strain is a pure one with main axes along the length and width of the specimen. The quantitative data for the experiments on the sample A of a woven fabric are collected in Table III With regard to rib knitted fabrics only one sample was investigated and for this the extensibility was a minimum in the direction of the wales and a maximum in that of the courses, and by virtue of this alternation of maxima and minima one need not expect any further extreme values In fact in the experiments none was found Photographs are not reproduced here but the quantitative data are given in Table V

For all the samples of woven and knitted fabrics the set of special directions along which the main axes of stress and strain are parallel (no evading action) must be identical with the set of directions along which the extensibility has an extreme value

All materials which are isotropic in their natural state*, show in stressed and strained states a relationship between the stress and strain such that the directions of their main axes coincide Here, therefore, there will be no evading action under simple pulls, and no rotation, as each specimen can suffer only a pure strain, with extreme changes of length occurring actually along the two directions of the main axes of the pull, i e lengthwise and widthwise in the specimen

Even in this case, however, the specimen will exhibit a Poisson effect which reveals a disparity between the corresponding main values of the stress and strain

The above-mentioned features have been confirmed experimentally

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* At rest and free from mechanical actions

(4) Relationship between Stresses and Strains in Textile Fabrics under a Simple Pull

This section contains a brief account of the theory of the quantitative evaluation of the relationship between stresses and strains in textile fabrics under a simple pull The data are derived from the pattern of markings imprinted on the specimen in the initial position.

The stress, i e the simple pull, has in the fabric a certain direction which is marked by the central line and which is specified by the bias angle between this line and the warp direction marked with an arrow head The magnitude of the stress is not shown in the marking.

The strain requires a more detailed description which is given for the initial and terminal positions in terms of the classical theory, in terms of the trellis model and in terms of the structure of the fabric by the warp and weft changes. The parameters specifying such a description are implicit in the patterns of marking, but the explicit evaluation requires either numerical calculation or graphical constructions

The graphical construction is illustrated in Figs 7(e) and (f) where M_0 and M are the central points, H_0J_0 and HJ the direction of pull, and the subscript zero refers in all symbols to the initial position and symbols without a subscript to the terminal position

For ease of identification dotted lines are used for the strain ellipse (P_0 and P), chain lines for the reciprocal strain ellipse (Q_0 and Q) and thick full lines for the lines of zero elongation ($R'_0R''_0$ and $R'R''$)

Figs 7(a) and 7(b) show respectively in the initial and terminal positions, the markings on the specimen, namely, the central point, the strain ellipse and the arbitrary direction fixed in the medium (U_0V_0 and UV) This latter is marked with an arrow head and corresponds to the warp direction in the fabric.

The transfer from any marking in any one position to the corresponding marking in the other position will be based on the principle that the coordinates of any point have the same value in the two positions when the axes of coordinates are chosen along the lines of zero elongation

For the full specification of the strain it is necessary to complete the patterns in the two positions The first stage concerns the terminal position as shown in Fig 7(d). On the strain ellipse (P) a concentric unit circle (Q) is superposed, to represent the reciprocal strain ellipse The points of intersection between the two curves of second degree determine the lines of zero elongation (R′ and R″) and the bisectrices of the angles between these lines determine the magnitudes and directions of the main axes of the strain ellipse Finally two radii of the strain ellipse are drawn along the warp and weft directions and also two tangents parallel to the radii These lines have been omitted from the figure in order to avoid overcrowding.

The second stage concerns the initial position The unit circle (P_0) representing the strain ellipse is already shown and the pattern is completed by the use of the principle of transfer explained above for some selected points

The point of intersection between the strain ellipse and the direction of pull is seen in the two positions as L_0 and L respectively, and the coordinates along the lines of zero elongation are known in the terminal position as ML′ and ML″ If then one constructs the triangle $M_0L_0'L_0$ on the base M_0L_0 with sides M_0L_0' and L_0L_0' equal respectively to ML′ and LL′, and similarly the triangle $M_0L_0''L_0$, one obtains in the initial position the lines of zero elongation (R_0' and R_0'') along the lines M_0L_0' and M_0L_0'' The reciprocal strain ellipse is then constructed from its main axes M_0X_0 and M_0Y_0 which are formed by a transfer of the points X and Y in the manner explained for the point L.

Finally one has to draw along the warp and weft directions two radii of the unit circle which represents the strain ellipse, and two tangents parallel to the radii.

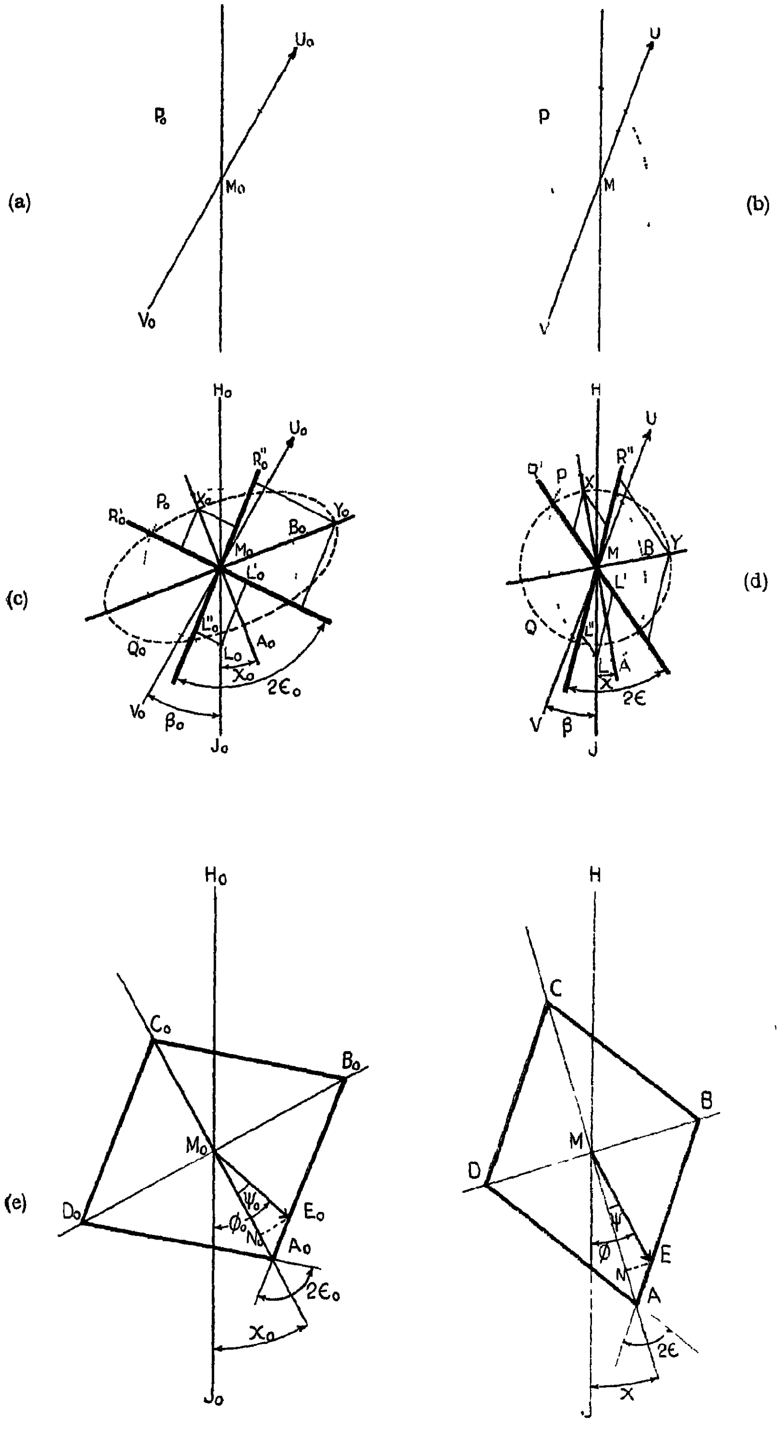
(a)
(b)
(c)
(d)
(e)
U_0
P_0
M_0
V_0
U
P
M
V
H_0
R_0''
R_0'
X_0'
Y_0
B_0
L_0'
L_0''
Q_0
L_0
A_0
χ_0
$2\epsilon_0$
β_0
J_0
H
Q'
R''
X
Y
B
L'
L''
Q
L
A
χ
2ϵ
β
J
C_0
D_0
E_0
N_0
ψ_0
ϕ_0
C
D
E
N
ψ
ϕ

Fig 7

The complete patterns exhibit for the two positions all parameters required for the full specification of the strain, and these parameters can now either be measured up or calculated trigonometrically from a rhombus of sides of unit length parallel to the lines of zero elongation as shown in Figs 7(e) and 7(f)

It has been found convenient to measure directly in the pattern the trellis characteristics of the strain, i e. the orientation of the trellis lines in the two positions as given by the opening angles of the trellis ($2\epsilon_0$ and 2ϵ) which diminish by the strain and the angle of evasion (χ_0 and χ) with $2\epsilon_0$ and 2ϵ equal respectively to $R'_0M_0R''_0$ and $R'MR''$ and χ_0 and χ equal to $A_0M_0J_0$ and AMJ respectively (Fig 7(c) and 7(d))

Then the classical strain characteristics, i e. the values and orientations of the main axes of strain, were deduced algebraically As the diagonals of the rhombus change from 2 cos ϵ_0 and 2 sin ϵ_0 to 2 cos ϵ and 2 sin ϵ the values of the main axes (a and b) are found as.

$$a = \frac{\cos \epsilon}{\cos \epsilon_0} \tag{1}$$

$$b = \frac{\sin \epsilon}{\sin \epsilon_0} \quad . \tag{2}$$

while the orientations with respect to the length direction of the specimen are specified by the angles of evasion χ_0 and χ and (χ_0+90) and $(\chi+90)$ respectively.

Finally the characteristics of the strain in terms of the changes in warp and weft were derived Taking first an arbitrary vector in the two positions M_0E_0 and ME, respectively, one denotes the angles ($E_0M_0J_0$ and EMJ) between the vector and the direction of pull by ϕ_0 and ϕ and the angles ($E_0M_0A_0$ and EMA) between the vector and the major axis of strain by ψ_0 and ψ. Consider the triangles $M_0E_0A_0$ and MEA, and note that the lengths of the sides along the lines of zero elongation must be equal ($A_0E_0 = AE$), and that the strain changes in length all lines in the directions of the main axes in the ratio a 1 and $b:1$, respectively The changes in orientation of the vector are then given by

$$\frac{\tan \psi_0}{\tan \psi} = \frac{\tan(\phi_0-\chi_0)}{\tan (\phi-\chi)} = \frac{a}{b} \quad . \tag{3}$$

The change in length (that is the elongation, λ) of the vector is given by

$$\lambda = ME - M_0E_0 = \frac{MN}{\cos (\phi-\chi)} - \frac{M_0N_0}{\cos (\phi_0-\chi_0)} = \frac{a \cos (\phi_0-\chi_0)}{\cos (\phi-\chi)}$$

and in combination with (3), λ is found in the initial position

$$\lambda = \sqrt{a^2\cos^2(\phi_0-\chi_0) + b^2\sin^2(\phi_0-\chi_0)} \tag{4}$$

and in the terminal position

$$\lambda = \frac{ab}{\sqrt{b^2\cos^2(\phi-\chi) + a^2\sin^2(\phi-\chi)}} \tag{5}$$

The changes in the density of a series of lines parallel to the vector are then found from the formula

$$\frac{1}{d^2} = \frac{1}{a^2\sin^2(\phi_0-\chi_0)} + \frac{1}{b^2\cos^2(\phi_0-\chi_0)} \quad . \tag{6}$$

Now the warp threads have, in the two positions, an orientation which is specified with respect to the direction of pull of the specimen, by the angles ϕ_0 and ϕ equal to the bias angles β_0 and β

The changes in the warp are then deduced from the equations (3 to 6) by substituting β_0 and β for ϕ_0 and ϕ.

A similar treatment can be used to give the changes in the weft

For purposes of cross checking one deduces from (1) and (2)

$$\tan \epsilon_0 = \sqrt{\frac{a^2-1}{1-b^2}}$$

$$\tan \epsilon = \frac{b}{a}\sqrt{\frac{a^2-1}{1-b^2}} \qquad . \qquad . \quad (7)$$

and from a comparison of the rhombus in Fig 7(e) and that in Fig 7(f)—

$$\frac{\tan \epsilon_0}{\tan \epsilon} = \frac{\tan \chi}{\tan \chi_0} = \frac{a}{b} \qquad . \quad . \qquad (8)$$

(5) Application of a Trellis model to Represent the Experimental Results

According to the theory it is possible to represent by a trellis model the experimental results obtained in a specimen of fabric which is strained from an initial to a terminal position by a simple pull of given direction and amount The trellis consists of two intersecting series of straight rigid rods which are pivoted to one another at the crossing points by pinpointed joints It will serve as a model when it is adjusted to the experimental conditions such that in either position its pinpointed joints coincide with the nodal points* of the yarns in the specimen, and its series of rods extend in the directions of the lines of zero elongation, which are not necessarily aligned with the directions of the yarns

For the adjustment it is necessary to ascertain by preliminary experiments the directions of the lines of zero elongation in the initial position, and the elongation lengthwise which the specimen suffers in the direction of the pull during the transition from the initial to the terminal position The model can then be correctly set in the initial position and will reach the correct terminal position in an experiment in which a pull applied to the model stretches it lengthwise to the predetermined elongation

In such an experiment the behaviour of the model accounts directly for the behaviour of the specimen with regard to all characteristics of the strain from the initial to the terminal position The characteristics include those discussed in the sections dealing with the pinpointing, linearity, Poisson effect and evading action, and those which refer to the shape and area of the specimen, to the yarn structure, to the pattern of markings imprinted on the specimen in the initial position and to any other pattern so imprinted.

A rigorous check was made for all the above-mentioned characteristics of the strain in order to ascertain the degree of conformity between the hypothetical experiment on the model and the actual experiment on the specimen This check was made by deducing all the theoretical characteristics (Th) of the strain from the appropriate trellis model and comparing these with the observed data (Ex). An example is given in Table II for fabric I and in general the agreement is within the experimental error introduced

Figs 8(a) and 8(b) illustrate diagrammatically the experiment on the trellis model for a general case, that is for an arbitrarily chosen direction of pull in an anisotropic material, such as the specimen of fabric under consideration The illustrations show the direction of pull as a line bearing an arrow head, and the trellis model as a representative rhombohedral cell, or rhombus for short, which can be made up from four straight rigid rods pivoted to one another at the corners of the rhombus * It will be noted that the diagonals of the rhombus are the directions of the main axes of strain, i e the directions along which the maximum changes in length occur. In the initial position the model and the direction of the intended pull are given as indicated in Fig 8(a), with the directions of the diagonals of the rhombus inclined at arbitrary angles to the direction of the pull in accordance with the requirements of the general case. If then the pull is applied the model will suffer a strain, and will reach a terminal position, as indicated in Fig 8(b), when the elongation of the model in the direction of the pull has reached the amount observed in the specimen A comparison between the Figs 8(a) and 8(b) reveals the various characteristics of the strain The characteristics of pinpointing and linearity are seen for the trellis lines in the maintenance of their points of intersection and of their straight linear form, while the characteristics of the Poisson effect are recognised by the changes in length parallel and perpendicular to the direction of pull (that is lengthwise and widthwise in the specimen) these changes being coupled As in the initial position of the rhombus there is an angle between the direction of the intended pull and the direction of the diagonal which can suffer the maximum elongation, the strain resulting from an applied pull shows the characteristics of an evading action with the rhombus suffering, in transition to the terminal position, a pure strain and a rotation In this pure strain the rhombus suffers a change in shape, with maximum elongation occurring at an "angle of evasion" to the pull along one diagonal and maximum contraction occurring along the other diagonal. In the rotation the diagonals of the rhombus are turned relative to the direction of pull by an angle of rotation, in such a way as to diminish the angle of evasion from the initial to the terminal position Thus the model accounts for the pinpointing, linearity, Poisson effect, and evading action. Moreover the model will change any point fixed on it in the one position, to the corresponding point in the other position in accordance with the principle of transfer given in the preceding section, and so account, without calculation, for the changes in the yarn structure, in the pattern of markings, and in any other pattern imprinted in the initial position

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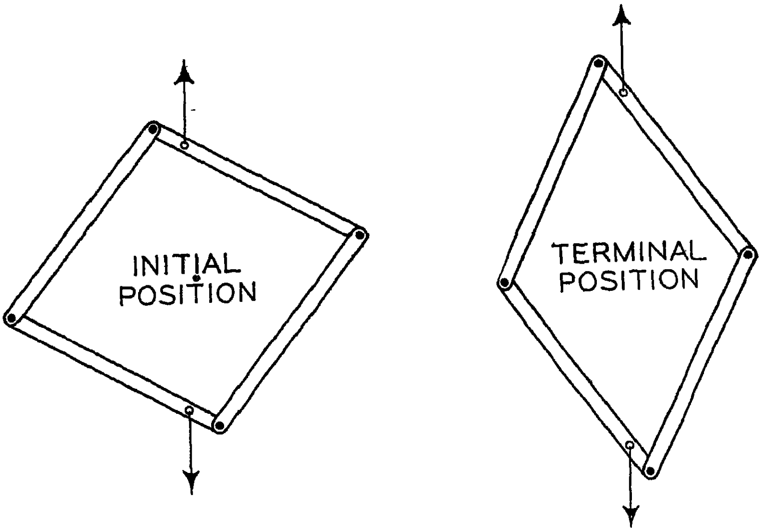
* A model with pinpoints coinciding with every nodal point of the fabric or with an arbitrary selection of them would in general have crossing points not coinciding with nodal points (complete coincidence would only be possible if the lines of zero elongation lay along the yarn directions) It is possible, however, to make a selection of nodal points giving as close a coincidence as desired with a complete set of pinpoints



(a) Fig 8 (b)

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* A model of this type was made from a "Meccano" set and used for experiments as described above

Finally, the model accounts simultaneously for the trellis characteristics of the strain, and for the classical ones, as well as those given in the terms of the yarn structure

The practical value of the trellis model is considerably enhanced still further by the empirical fact that in all the specimens of textile fabrics under examination, the trellis characteristics calculated for the initial position vary only slightly with the amount of pull.

A detailed examination of all the experimental results shows that with increasing amounts of pull there is a slight change in both values, ϵ_0 and χ_0, and this change is small (less than about 3°) except for some specimens of crêpe and knitted fabrics (samples K and F), where for stretches over 25 per cent , larger variations are found, up to about 12° The variation in the trellis characteristics ϵ_0 and χ_0 is, in fact, so small as to be negligible for many practical purposes, and then it is possible to use in the initial position of any given bias specimen the same trellis model for all amounts of pull applied The model here envisaged will be an average one. Its opening angle and evasion angle in the initial position, with values $\bar{\epsilon}_0$ and $\bar{\chi}_0$ say, will conveniently be calculated from the arithmetical means of the values ϵ_0 and χ_0 which are observed for different amounts of pull A typical example of the agreement reached by using a single trellis model for all amounts of pull is shown in Table II for a specimen of fabric I, which has been subjected under a bias angle of $-22\frac{1}{2}°$ to different amounts of pull by roller grips and trellis grips The agreement is seen from a comparison between the columnar subdivisions marked Ex and Th which correspond respectively to the actual observed values of the strain and those calculated from the model with average characteristics $\bar{\epsilon}_0$ and $\bar{\chi}_0$.

The use of the same trellis model in the initial position for different amounts of pull is particularly convenient when it is required to test a specimen of fabric in trellis grips. In such tests the grips may be set in the initial position once and for all at the angles ϵ_0 and χ_0, determined from preliminary experiments on roller grips, and a series of states of strain which are sensibly homogeneous over the whole area of the specimen may be produced by gradually increasing the amounts of pull applied Examples of such tests are shown in the Plates III and IV. Plate III refers to roller grips in which different samples of fabrics have been tested under bias angles of $-22\frac{1}{2}°$ with various amounts of pull. For each specimen the average characteristics of the trellis were calculated for the initial position and trellis grips (angle or parallelogram) were then set accordingly Plate IV shows the results obtained for various amounts of pull with these settings. The absence of appreciable " waisting " or " buckling " in the specimens confirms the applicability of the same trellis model for all amounts of pull

Having disposed of the slight variation of the trellis model with the amount of pull applied, this variation will now be neglected and the constitutional significance of the model brought out by studying its variation with the structure of the bias specimen under investigation

(6) Structural Significance of Trellis Model in Textile Fabrics

The structural elements of the trellis model, that is the two series of straight rigid rods, and the pinpointed joints which link the rods to one another, are associated in a certain way with the yarn structure of the fabric Attention has already been drawn to the fact that the pinpointed joints of the model can be identified with the nodal points of the yarns since these points are maintained intact throughout all the experiments It thus remains to investigate here the relation between the rigid rods in the model and the yarns in the specimen of fabric

Suppose that two corresponding experiments are made by applying simple pulls to a specimen of fabric and to the appropriate trellis model In these experiments the specimen and the model are assumed to lie in the same plane, and in it one may represent the specimen by two intersecting series of straight lines drawn along the yarn directions, and the model by two similar series of lines drawn along the rigid rods in the directions of zero elongation

When a simple pull is applied and corresponding states of strain are obtained in the specimen and in the model it is found that the characteristics of pinpointing and linearity, discussed in the preceding sections, allow the strain to be produced only by certain mechanisms In the specimen two mechanisms are allowed,

(*a*) a trellis mechanism which produces a strain merely by a change in orientation of the representative lines, their length being maintained constant, and

(*b*) a stretching mechanism which produces a supplementary strain merely by a change in length of the representative lines, their orientation being maintained constant

Mechanisms (*a*) and (*b*) will in general make their contributions to the total strain since there is nothing to prevent the occurrence of a change in orientation and in length* of the lines which represent the yarns of the fabric

In the model, on the other hand, only mechanism (*a*) is allowed while (*b*) cannot operate since the representative lines are here defined as lines of zero elongation

In Tables II to VII are given the experimental data concerning the changes in all the representative lines of the specimens and of the models For the specimens the contributions made by the two mechanisms are separated and tabulated respectively under the headings *Orientation,* and *Length of Warp and Weft* or of *Wales and Courses* It is seen that both contributions depend in general on the structure of the specimen and on the direction (bias angle) For the model there is only the mechanism (*a*) operative and its contribution is recorded under *Orientations of the Lines of Zero Elongation*

For the discussion of the experimental evidence first visualise an idealised fabric with warp and weft threads, or wales and courses so inextensible that the fabric is inextensible along the directions of the representative lines of these elements Here, then, the inextensibility will prevent the mechanism (*b*) from operating, and will allow only the mechanism (*a*) in which the lines representing the yarns of the fabric will coincide with those representing the trellis lines of the model Here the structural significance of the model is evident There is a complete coincidence between the representative lines of the structural elements of both the ideal fabric and the model, and this coincidence is independent of the bias angle, the amount of pull, the structural details of the fabric, etc

The actual fabrics under investigation deviate from the idealised kind discussed above to a greater or less degree in accordance with the amount of extensibility which they permit in the directions of the lines that represent their structural elements Here the structural significance of the model is less obvious and requires detailed examination which, must cover in principle the initial and terminal positions It suffices, however, to consider the initial position only, since similar considerations apply to the terminal position

Having disposed in a preceding section of the slight variation of the trellis model with the amount of pull applied this variation will now be neglected and the structural significance of the model brought out by studying the variation of the model with the direction of the pull, that is with the bias angle of the specimen It will be advantageous for a detailed discussion to classify the fabrics with regard to the magnitude of the contribution made by mechanism (*b*) Two widely separated classes are obtained containing respectively the different varieties of woven and of knitted fabric

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* The change in length of the representative lines of the yarns is due to a large extent to a change in crimp and only to a comparatively small extent to a change in length of the actual yarn In general, there is a crimp interchange, one set of threads increasing in crimp, and the other decreasing

Consider first the woven fabrics Here the extensibility under pulls in the various directions shows a characteristic distribution over the full circle of bias angles The distribution is symmetrical to the warp and weft directions (in accordance with the structural symmetry of the fabric) and the value of the extensibility changes with the bias angle in a wave-like form, passing through sharp troughs with minimum values at the bias angles corresponding to the directions of warp and weft, and passing through flat crests with maximum values at bias angles near to, or coinciding with, the bisectrices of the angles between the warp and weft directions The full circle of bias angles may thus be divided roughly into two complementary sets of sectors, corresponding respectively to the troughs and the crests of the wave. One set of sectors with small values of extensibilities (corresponding to the sharp troughs of the wave), consists of four narrow sectors which are centred on the directions of warp and weft, and a pull here produces a strain by operating mainly mechanism (*b*) there being appreciable changes in length along the two yarn directions and smaller or zero changes in the angle between these directions The other set of sectors with comparatively large extensibilities (corresponding to the flat crests of the wave), consists of four wide remaining sectors that are centred on the directions near to or coinciding with the bisectrices of the angles between the warp and weft directions, and here a pull produces a strain by operating mainly mechanism (*a*) there being appreciable changes of the angle between the two yarn directions When the trellis models in the initial position are constructed for the various bias angles the structural significance of the model is shown by comparing the directions of the trellis lines with the directions of lines drawn on the fabric along the yarn directions The significance is hardly noticeable in the first set of sectors where the mechanism (*b*) predominates but is well in evidence in the second set of sectors where the mechanism (*a*) is of primary importance. Here there are two directions of pull, near to or coinciding with the directions of the bisectrices of the angles between the warp and weft directions, where the mechanism (*b*) does not operate at all and for these directions of pull one trellis line can be identified with the warp, and the other with the weft As the bias angle is changed and the direction of pull deviates towards one or the other of the yarn directions, the mechanism (*b*) gains in importance, but as long as the variation of the bias angle remains within one of the sectors of the second set it is found that the directions of the trellis lines are almost invariantly fixed in the fabric, one remaining near to the direction of the warp, and the other near to that of the weft. Only when the bias angle is changed further, and the direction of the pull chosen in one of the sectors of the first set, will there be an appreciable deviation between the direction of the trellis lines, and those of the warp and weft, and this deviation will first increase, then reach a maximum when the pull is along the warp or weft direction, and finally decrease again when the direction of pull passes over a yarn direction (from one quadrant into the next one) When the deviation is at its maximum value, corresponding to a pull along one of the yarn directions, the trellis-lines will be symmetrically orientated to the warp and weft directions so that it will here be completely arbitrary which trellis line is associated with the warp and which with the weft* On either side of the maximum deviation there is a well-defined association and it is noted particularly that there is a change over in the mode of association as the direction of pull passes over a yarn direction such that the trellis line previously associated with the weft say, will now become associated with the warp and *vice versa*

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* In general, a pull along one yarn direction produces changes in length along both yarn directions, and these changes are due mainly to a crimp interchange between the two sets of yarns producing an elongation in the direction of pull and a contraction at right angles to this direction, while the changes in the actual lengths of the yarns are very small.

Owing to the similarity in behaviour found for woven fabrics of different structural details, it will suffice to consider one of them only, and sample A is selected as a typical one The results obtained for this sample in simple pull experiments are shown in Plate I and Table III

On comparing the angles of orientation of the trellis lines, $(\bar{\chi}+\bar{\epsilon}_0)$ and $(\bar{\chi}-\bar{\epsilon}_0)$ with those of the warp and weft it will be seen from Table III that the deviation is small over a wide range of bias angles at either side of the -45° direction, and increases suddenly to appreciable values as one approaches the warp or weft direction The fabric, so to speak, is very quick to seize any opportunity of yielding to the pull by changing the angle between warp and weft [mechanism (*a*)] in preference to changing the length or crimp of the yarn [mechanism (*b*)]

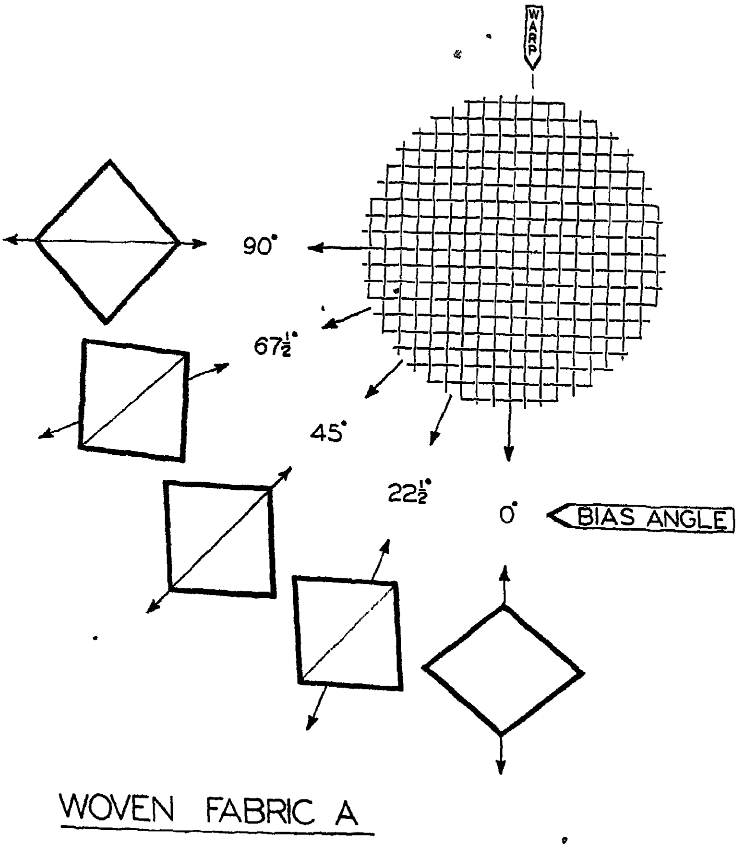

Fig 9

The relationship between the trellis lines and the directions of the yarns is shown diagrammatically in Figs 9 and 10

In Fig 9 the structure of the fabric is represented in the initial position, by two sets of lines drawn along the warp and weft directions in a circular space at the right hand upper corner The lengthwise directions of the specimens, along which the pull is applied, are represented for various bias angles by arrows drawn on radial lines from the centre of the circular space, each arrow being labelled with the appropriate value of the nominal bias angle For each such angle the trellis model is shown as a rhombus centred on the corresponding radial line at a constant distance from the centre of the circular space The thick full lines forming the sides of the rhombus give the directions of zero elongation, and the diagonal drawn as a thin full line represents the direction of the major axis of the strain Attached to the sides of the rhombus are two oppositely directed arrow heads drawn in the direction of the pull The trellis characteristics, that is the opening angle $\bar{\varepsilon}_0$ and the evasion angle $\bar{\chi}_0$ appear here as the angles which the drawn diagonal makes, respectively, with one of the adjacent sides of the rhombus and with the indicated direction of pull The experimental results cover a range of bias angles of only 90°, and only their range is shown here However, since the structure of the cloth is symmetrical with respect to the warp and weft directions it would be a simple matter to extend the diagram to cover the full circle of bias angles In fact the complete diagram may be seen by placing two mirrors with their planes normal to the plane of the paper along the lines corresponding to the bias angle of 0° and −90° so as to embrace the quadrant covered by these angles This figure shows very clearly the approximate coincidence in direction of the trellis lines and the warp and weft, over the range of bias angles from about −22½° to about −67½°, and the deviation over the remaining ranges It also shows the symmetry of the trellis lines with regard to the warp and weft directions for the bias angles 0° and −90° The change over in the mode of association between the trellis lines and the warp and weft directions as we pass through either the 0° or −90° bias angle, can be visualised by considering that when the bias

WOVEN FABRIC A

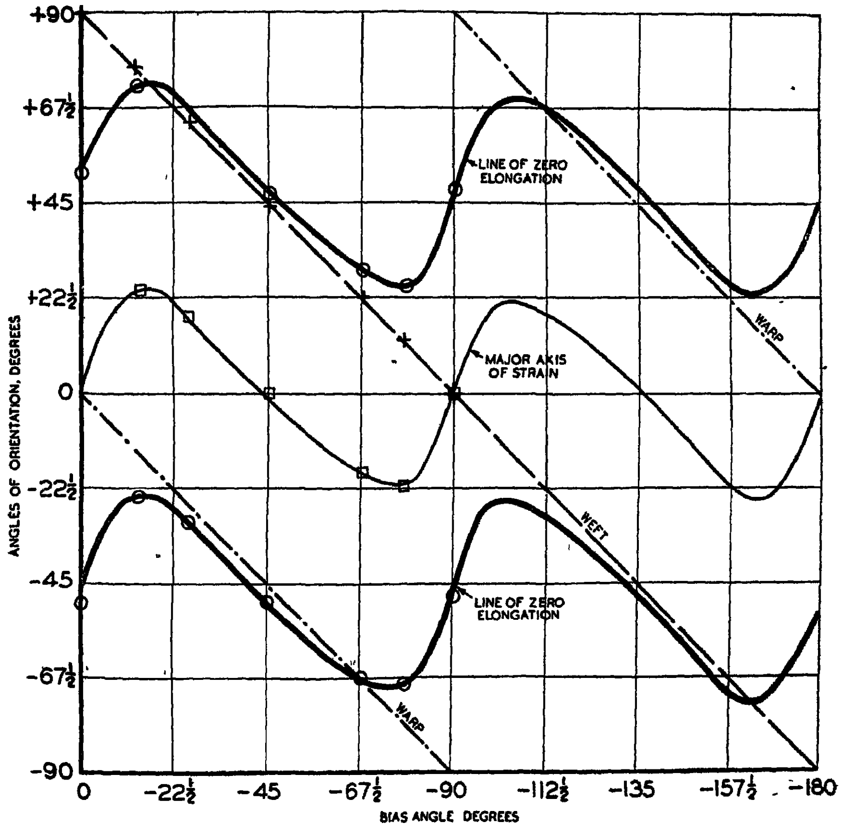

Fig 10

angle changes continuously from −45° to +45° say, any one trellis line will rotate continuously through 90° relative to the yarn structure, so that if it coincided at a bias angle of −45° with the warp, say, it would coincide for +45° with the weft. The change over in the mode of association is seen more directly in Fig 10

In Fig 10 are plotted, from the results shown in Table III, the angles of orientation of the two trellis lines and the warp and weft against the bias angle over the range 0° to −180°

On considering the complete conceivable range of values of the angles it will be seen that the diagram repeats in both directions with a period of 180°, and that Fig 10 represents a single period in a square of side 180° The orientation of the warp is by definition equal to the bias angle so that the corresponding graph labelled "Warp" is simply a repeat of a straight line at −45° with the axis of abscissæ, passing through the point (0°, 0°) Similarly the graph for the weft is a periodic repeat of a line of the same slope passing through the point (0°, 90°) In the selected square, the graph of the warp shows two portions of the periodic repeat, one passing through the point (0°, 0°) and the other through the point (−90°, +90°), while the graph for the weft shows only one portion passing through the point (0°, 90°) The graphs for the trellis lines are shown as continuous curves, each labelled "Line of Zero Elongation,"[*] and each such graph has a wave-like form which approximates in successive quadrants alternately to the graphs of warp and weft over a considerable range of bias angles, centred about the −45° and −135° bias angles, and deviates abruptly from the graphs of the warp and weft in comparatively small ranges, centred about the 0° and −90° bias angles, where the change in the mode of association occurs. In the diagram is also plotted the graph for the major axis of the strain, which is midway between the graphs for the two trellis lines, the major axis being the bisector of the trellis lines This graph shows directly the angle of evasion as a function of the bias angle, and the opening angle of the trellis is exhibited as the distance along the ordinate axis between this graph and that of one of the trellis lines.

Consider now the knitted fabric F, results for which are shown in Plate II and Table V The extensibility under pull shows over the full circle of bias angles a distribution of values of a wave-like form which is symmetrical to the yarn directions, but essentially different from that described for woven fabrics Whereas in the woven fabrics both the yarn directions have minimum extensibility, in the sample F of the knitted fabric it is found that only one direction that of wales, corresponds to a minimum of extensibility, whilst the other, that of the courses, corresponds to a maximum Moreover, neither the minimum nor the maximum is very pronounced, the extensibility varying only slightly with the bias angle, and the material therefore approximating in its behaviour to that of an isotropic medium Thus, the sample F of the knitted fabric has a wave-like curve of extensibilities which differs from that of a woven fabric, with respect to the number per full circle of bias angles, of the crests and troughs of the wave, with regard to their location relative to the yarn structure, and with regard to their form, that is the sharpness or flatness of the crests and troughs This difference between the woven fabrics and the knitted fabric F shows up by the difference in kind and degree of the association of the yarn structure and the trellis model It is seen from Table V that in the knitted fabric F an association between the trellis lines and the wales and courses occurs only for one yarn direction, namely that of the wales, and this association is less close than the corresponding association in a woven fabric In each quadrant one of the trellis lines is near to the direction of the wales for all bias angles, except when the pull approaches the direction of the wales or courses, and here the deviation becomes marked and the mode of association changes from one trellis line to the other. A sectional division of the full circle of bias angles leads, for the sample F of knitted fabric, to two complementary sets of sectors, one set associated with the crests and the other with the troughs of the wave, but the division is not discussed in detail because it is less clearly defined than in the woven fabrics (both the crest and troughs being very flat), and accordingly it provides little help in the discussion of the experimental results.

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[*] The experimental data cover only the range of bias angles from 0° to −90°, but in virtue of the symmetry of the structure the complete diagram possesses twofold central symmetry about the point (−90°, 0°) and this allows the graphs to be constructed over the entire range

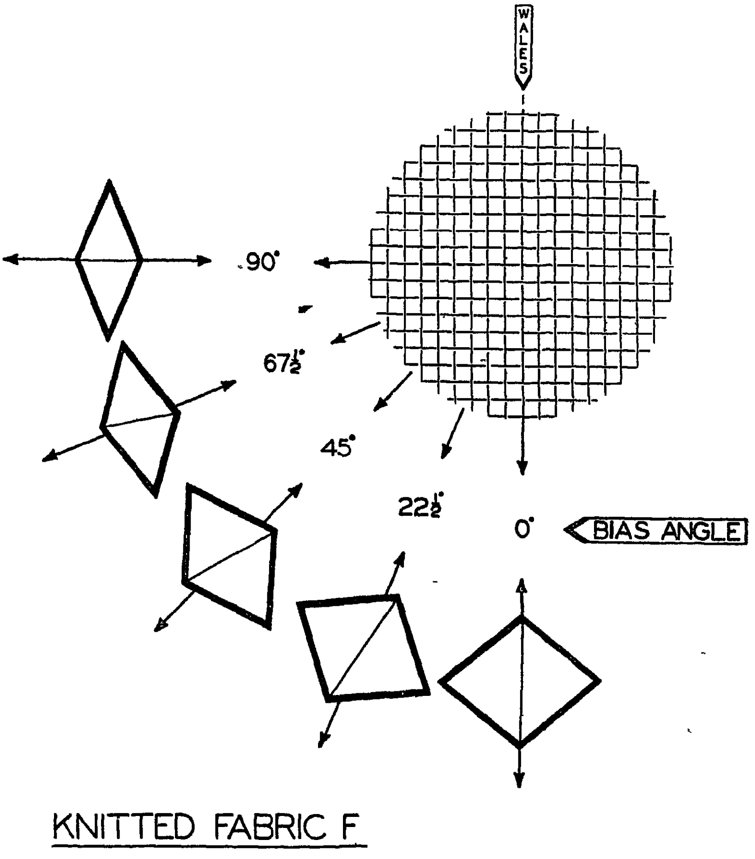

Fig. 11

In Figs. 11 and 12 are shown diagrammatically the association between the trellis lines and the directions of the yarns. The figures have been constructed similarly to those for the woven fabrics.

Fig. 11 shows* clearly the approximate coincidence of one of the trellis lines with the direction of the wales over a large range of bias angles from about −30° to about −80° and from about −100° to −150° and the merely incidental coincidence of the other trellis line with the direction of the courses at two bias angles near to −22° and −157°. It also shows over the remaining ranges the deviation of the trellis lines from the directions of the wales and courses, and the symmetry of the trellis lines with respect to these directions At the bias angle of 0°, that is when the pull is along the wales, the deviation of the trellis lines from the wales and courses is very marked, whereas at the bias angle of −90°, that is when the pull is along the courses, both trellis lines approximate to the direction of the wales The latter effect occurs because the whole system, including the trellis lines, is symmetrical with respect to the wales direction, and the bias angle lies in the centre of the range where there is approximate coincidence of a trellis line with the wales The mode of association between the trellis lines and the wales and courses changes over at the bias angles 0° and −90° The change over is similar in kind to that which occurs at 0° and −90° in the woven fabrics

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* We imagine the figure to be extended over the full range of bias angles by mirror reflections along the directions of the wales and courses.

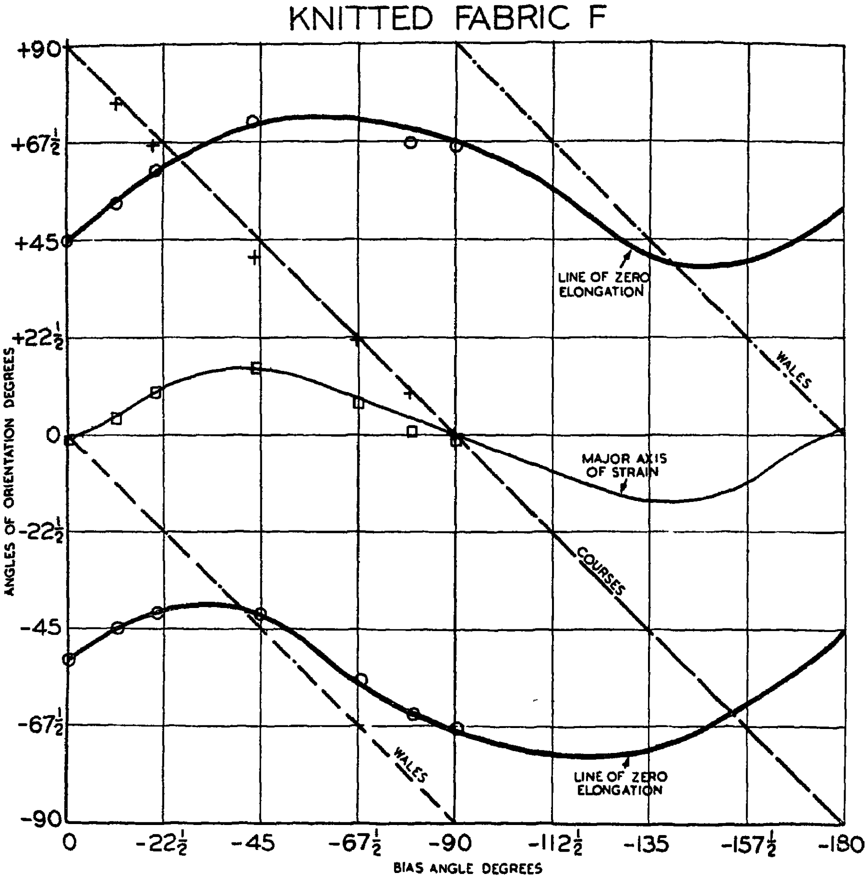

Fig 12

In Fig 12 the mode of association between the yarn structure and the trellis model may be seen by comparing the graphs which correspond respectively to the yarn directions marked " Wales " and " Courses ", with the graphs which correspond to the directions of the trellis lines, marked " Lines of Zero Elongation " The graphs for the trellis lines have a wave-like form and one can see that the graph of the wales is near to that of one trellis line in the range of bias angles between about −30° to −80° and near to that of the other in the range between −100° and about −150° The merely transitory coincidence of the trellis lines with the direction of the courses is seen by the almost perpendicular intersection of the graphs of the trellis lines with that of the courses which occurs at about −26° and

$-154°$. The change in the mode of association between the yarn directions and the trellis lines, which occurs at bias angles 0° and $-90°$, is shown by the fact that the graph of each trellis line intersects alternately the graph of the wales, and of the courses in successive quadrants The graph of the "Major Axis of Strain" has been plotted and this graph exhibits the trellis characteristics $\bar{\varepsilon}_0$ and $\bar{\gamma}_0$ as a function of the bias angle, in the manner described in connection with Fig 10

The experience gained on woven and knitted fabrics may be used to formulate some general principles about the structural significance of the trellis model for a given material.

(7) Description of Tables I to VII.

Table I refers to the structure of the fabrics used.

The layout of Tables II to VII in rows and columns was chosen in accordance with the experimental procedure and with the theory of trellis models In the experiments a specimen was prepared and mounted in its initial position, and a series of simple pulls of increasing amounts of stretched length was applied to it, giving the specimen in a series of terminal positions. The application of the trellis theory to the experimental results for a particular specimen enables calculations to be made of the various trellis models which lead respectively from the initial position to the various terminal ones

To make the tables correspond to the above considerations main rows have been allocated for the specimens at various bias angles For any particular bias specimen the first row corresponds to the initial position, and the subsequent rows correspond to the succession of terminal positions reached by the specimen under the application of simple pulls of increasing amounts All measurements of areas and lengths in a terminal position are expressed in percentages of the corresponding measurements made in the initial position and for convenience the initial position has been regarded as a terminal one having all measurements of 100 per cent All orientations of lines in any position are measured relative to the direction of the pull by angles which are reckoned as positive for clockwise deviation and negative for anti-clockwise deviation.

All data referring to the specimen are tabulated under four main columnar divisions which are divided and sub-divided successively, where necessary

The first main columnar division "Specimen in Initial Position" gives under "Material" and "Nominal Bias Angle" (where these vary) a description of the kind of fabric used in accordance with Table I, and the nominal angle at which the specimen was intended to be cut out of the sample (The angle is nominal since there is sometimes a slight deviation between the intended angle and the actual one[*]).

The second main division—"Simple Pull to Stretched Length", specifies the independent variable (i e the variable under direct control) for the series of simple pulls of increasing amounts Here the lengthwise extension produced by the pull has been listed and measured by the per cent stretched length of the specimen, since the magnitude of the forces involved are not of prime concern

The third main division—"Specimen in Successive Terminal Positions", specifies for these positions the various dependent variables which are of interest An elaborate sub-division was required in order to account for the great variety and complexity of the changes that take place It has not been practicable to reproduce here for every specimen the whole list of all the dependent variables which are of interest, and to account separately for their theoretical and experimental values Such a full account is therefore given only for the one fabric recorded in Table II Here are listed the dependent variables in five divisions, headed respectively—"Width", 'Area", "Structure", "Classical Strain" and "Trellis" Some of these divisions had to be sub-divided successively to isolate the different dependent variables from one another For ease of comparison two sub-columns are provided and headed Th and Ex referring respectively, to theoretical values deduced from the trellis theory, and experimental values observed on the specimen The theoretical values were calculated from the mean values of the opening angle and the evasion angle is given in the fourth main division The division "Structure" refers to the threads with two sub-divisions headed respectively "Warp" and "Weft" Each of these is further sub-divided for differentiating between "Length", "Orientation", and "Spacing" of the threads The division "Classical Strain" refers to the total displacement of the specimen from its initial to its terminal position and this is analysed in sub-divisions headed "Pure Strain", and "Rotation", the rotationless pure strain requires a further analysis with sub-divisions accounting for the "Major Axis" and "Minor Axis" of the strain ellipse, and further still for each of these axes for their "Length" and "Orientation" Finally, the division "Trellis" refers to the trellis and its characteristics are given in two subdivisions, headed respectively "Opening Angle" and "Evasion Angle"

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[*] The actual bias angle i e the actual orientation of the warp in the initial position is given in the first row of the third main column, under the heading "Warp" with sub-heading "Orientation"

The fourth main division—"Trellis Calculated for Initial Position" refers in that position to the calculated Trellis models which lead from the initial to the various terminal positions Each such model can conveniently be characterised by the two parameters, which are listed in the corresponding two sub-divisions under the headings, "Opening Angle" and "Evasion Angle" In each sub-column are given average values of the opening angle and trellis angle for the various amounts of pull on the same specimen in order to show the slight variations of these angles with the amount of pull applied.

Table II contains the results of a comparison between the theoretical and experimental values for the fabric I stretched at a bias angle of $-22\frac{1}{2}°$ in roller and in trellis grips

Tables III and V relate respectively to the woven fabric A and the knitted fabric F stretched at various bias angles in roller grips.

Tables IV, VI and VII relate to a variety of fabrics stretched under a bias angle of $-22\frac{1}{2}°$ respectively in roller, angle and parallelogram grips

In Tables III, IV, V, VI, and VII the list of dependent variables has been reduced and only the experimental values are recorded * Moreover, in the sub-division headed "Trellis" the experimental values of the angles formed by the lines of zero elongation and the directions of the pull instead of the opening angle and evasion angle, are given and are labelled "Lines of Zero Elongation" with two sub-headings "Orientation" All angles referring to Orientation, Rotation, Opening and Evasion are given in degrees, and are positive unless marked otherwise

We are indebted to Mrs Henry for the great care and accuracy with which she helped in evaluation, to Mr. C W. Bradley for help in the photographic technique, and to Mr G Grundy for preparing the drawings.

British Cotton Industry Research Association

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[*] The experimental values given in the tables are in good agreement with the theoretical ones deduced from the trellis model by calculation

[†] The columnar division headed (Table II) "Classical Strain" is headed "Deformation" in Table III-VII and gives only the characteristics of the pure strain.

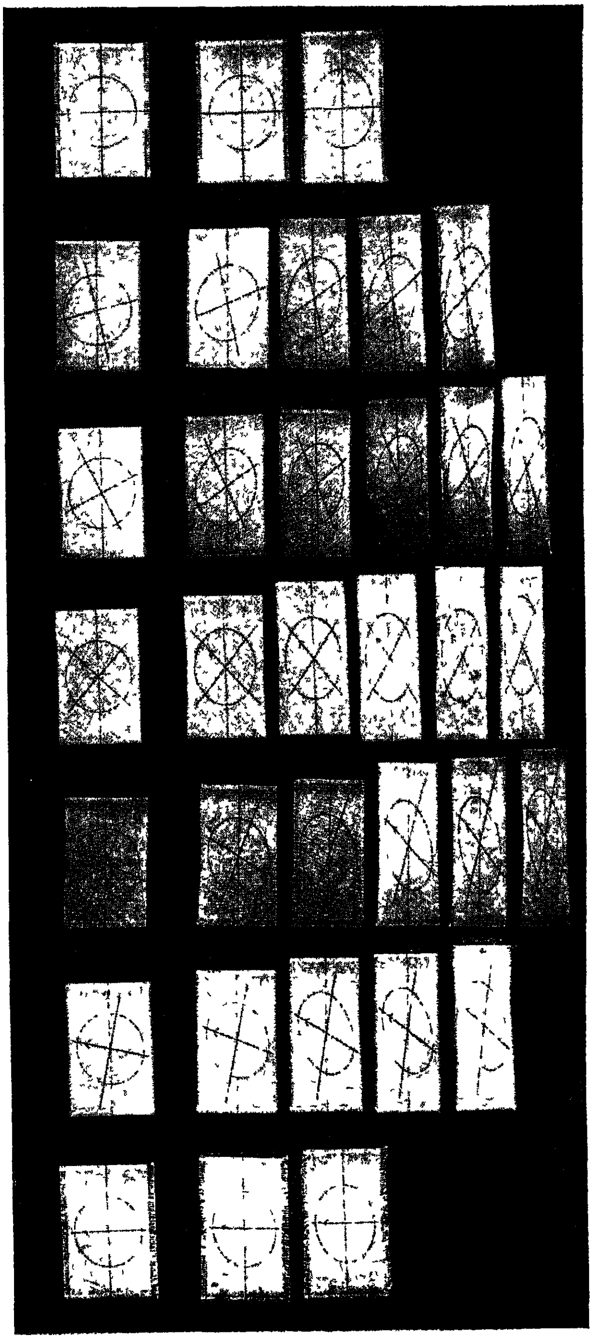

Plate I

Roller grip specimens Fabric A
Specimens cut out at various angles

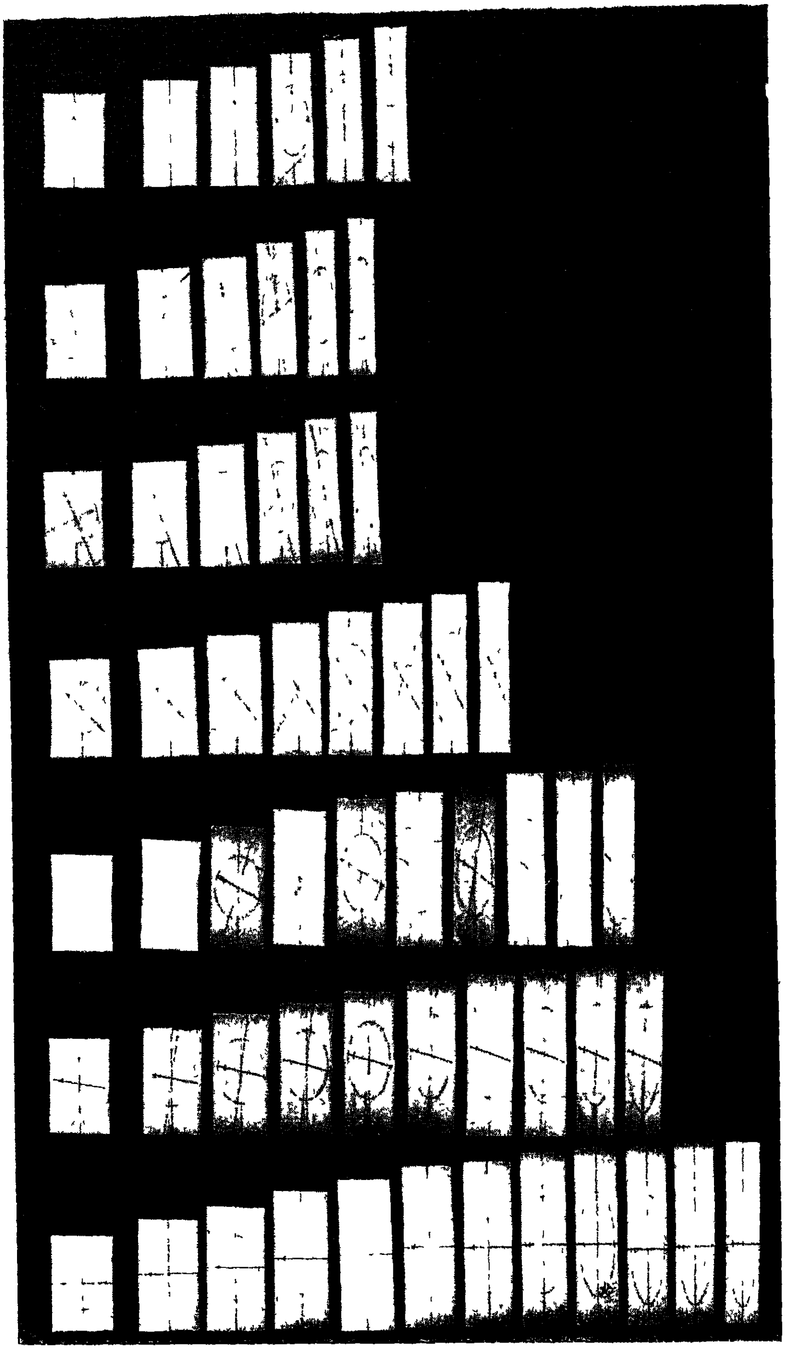

Plate II

Roller grip specimens Fabric F (Rib knitted) Specimens cut at various angles.

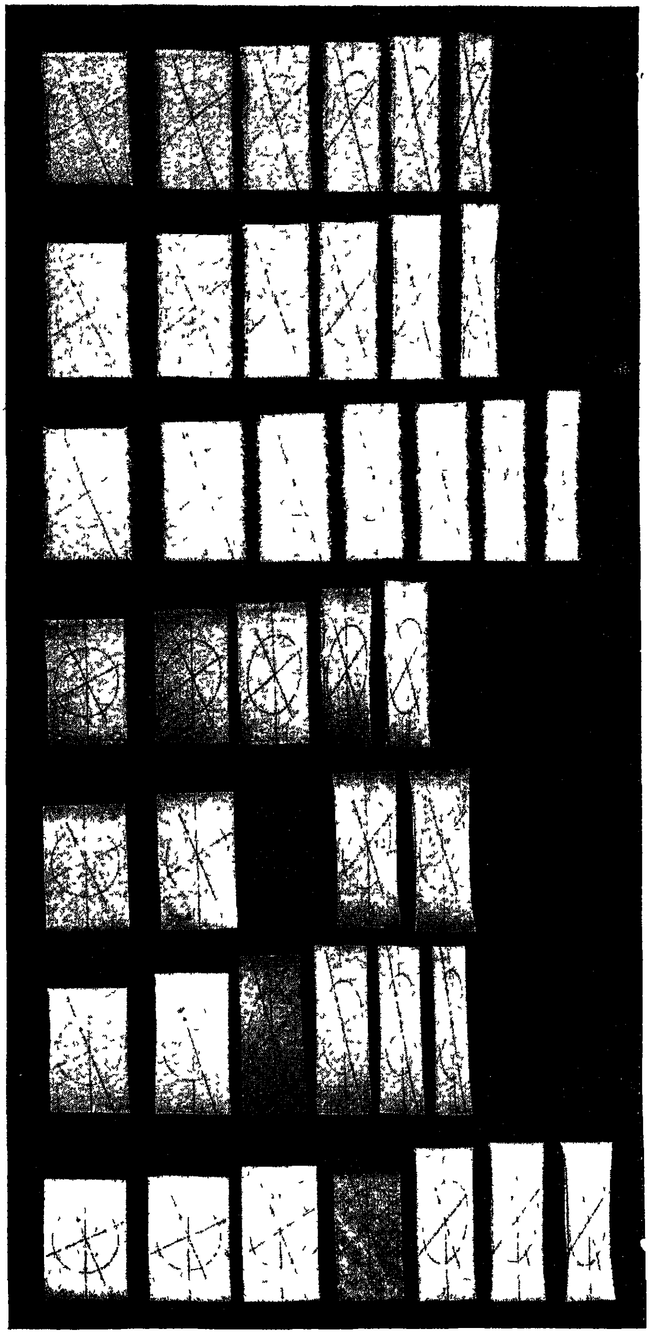

Plate III
Roller grip specimens

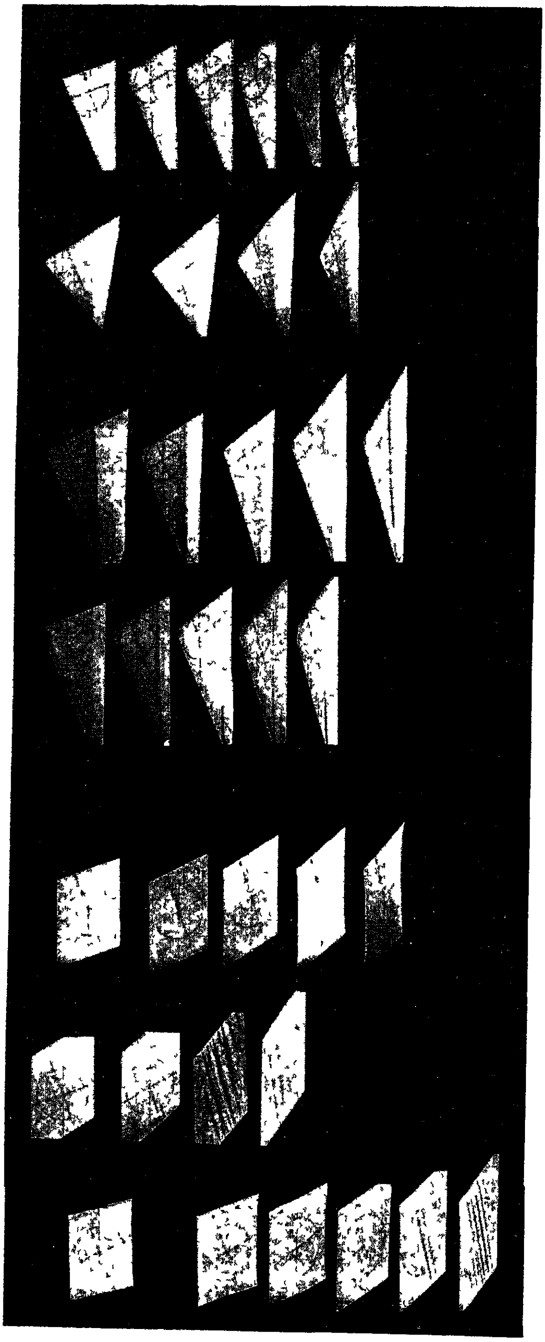

Plate IV
Top four Angle grip specimens
Bottom three Parallelogram grip specimens

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TRANSACTIONS

7—THE MOISTURE REGAIN OF SILK

i. ADSORPTION AND DESORPTION OF WATER BY SILK AT 25°C.

By E. A. Hutton and Joan Gartside

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I. INTRODUCTION

The relation between the moisture content of silk and the relative humidity of the atmosphere to which it is exposed has been given considerable attention by a number of investigators, with widely varying results.

Muller[1] made a series of estimations of the moisture contained in various textile fabrics compared with that present in the atmosphere and gave a formula which was said to express the regain at any temperature as a linear function of the relative humidity. Schloesing[2] studied the relation between moisture regain and the relative humidity of the air for Cevennes and China silks, both in the gum and after boiling-off, at temperatures of 12°, 24°, and 35° C The curves obtained are sigmoid in shape and show that at any given humidity and temperature the amount of water taken up is different for the two kinds of silk, whilst for the same kind of silk the regain is higher for the material in the gum than after degumming. The regain at a given humidity for any one silk was found to decrease with increase in temperature.

Scheurer[3] has given data on the comparative hygroscopicities of different textile materials at 100° C. and saturation point, and also at normal atmospheric humidities; he compared his results near saturation with values obtained by Levrat[4] at 25° C. The adsorption of moisture by a number of fibrous insulating materials has been investigated by Kujirai *et al*[5] over the range of 0 to 95 per cent. R.H. at 30° C and their results for silk give a curve of similar shape to those obtained by Schloesing. They refer to the presence of a hysteresis effect but no desorption values are given for silk.

Values for the regain of silk in the gum (Italian), degummed silk, and "bourette" at relative humidities between 30 per cent. and 100 per cent. are given by Honig[6] who found silk in the gum to have a lower regain than has degummed silk at corresponding humidities On the other hand, Obermiller and Goertz[7] agree with Schloesing that silk in the gum state adsorbs more water than does the degummed material at the same humidity. Their experiments, which were made on silk organzine (said to be probably of Italian origin) also showed that the regain of the material was reduced by a previous heating at 75-100° C

The British Silk Research Association (quoted by McBain[8]) also attribute a higher regain to silk in the gum than to the same silk after degumming. The moisture regains of degummed iso-electric Chinese, Japanese, and Italian silks are said to agree to within 0.1 per cent. but Tussah silk has a greater regain than mulberry silk. The regain was found to be greater during desorption than during adsorption. Similar results from the same laboratories are given in a brief note by Denham and Allen.[9]

According to Schaposchnikov,[10] observations on the moisture adsorption and desorption of vegetable, animal and artificial fibres extending over several months do not show any evidence of hysteresis. Some data for the adsorption of water by silk at various humidities are given by Oguri.[11] Carr[12] found that the regain of degummed silk was reduced by acetylation. Wiegerink[13] studied the moisture relations of silk at elevated temperatures (96-302° F). Adsorption and desorption curves for a purified sample of degummed silk at 25° C. are given by Goodings and Turl[14] who have also deduced the value of 35·8 per cent. for the regain at saturation from density and swelling data. Bull[15] found hysteresis between the adsorption and desorption regains of degummed silk and gives average values for temperatures of 25° C. and 40° C.

The present investigation was undertaken with the object of comparing the regain—relative humidity relations of Japanese, Chinese, and Italian silks both in the gum and after degumming at all humidities between 0 and 100 per cent. and to define the boundary curves for adsorption and desorption conditions for these silks.

II. EXPERIMENTAL METHODS

For most of the work described the vacuum adsorption apparatus devised by Urquhart and Williams[16] for their investigations on cotton has been used. A full description of the apparatus and procedure is given in the original account. Briefly, the apparatus consists of an adsorption bulb, containing the dry sample, connected to a manometer and to a graduated tube containing air-free distilled water, the whole being completely evacuated of air and maintained at a constant temperature (25° C.). By means of a tap between the adsorption bulb and the water tube a known amount of water is allowed to evaporate into the bulb and after equilibrium has been attained the pressure of water vapour is read on the manometer. Successive amounts of water are admitted to the bulb until the silk is saturated, the equilibrium pressure readings being taken after each addition The water tube is then cut off and in its place is sealed a tube with a ground-glass joint through which the sample bulb can be put into communication with an evacuated tube containing phosphorus pentoxide. The water is removed from the silk in stages, equilibrium pressure readings being taken as before until the silk has regained its initial dry state

When the volume (and therefore the weight) of water admitted to the silk at any stage is known, the weight of water taken up by 1 gram of dry silk is readily calculated. The percentage regain is obtained by multiplying this value by 100. Corrections are applied to the observed manometer readings to allow for the difference between the meniscus heights in the two limbs of the manometer and the relative vapour pressures are found by dividing the corrected pressures by the saturation pressure of water vapour at 25° C (23·78 mm.). The relative vapour pressure × 100 is equal to the percentage relative humidity of the atmosphere with which the silk is in equilibrium.

Each adsorption bulb contained 5-6 grams of silk. The silk was initially dried to constant weight in the bulb by evacuation at room temperature, a phosphorus pentoxide tube being inserted between the bulb and the pump In the early stages of the work some difficulty was encountered in removing the last traces of air from the silk. This residual air was apparently displaced from the silk when water vapour was admitted and was revealed at the end of the adsorption experiments by the fact that the final pressure attained was greater than the saturation pressure of water vapour. To overcome this difficulty the bulb containing the silk was evacuated for several days and sufficient air-free distilled water to saturate the silk was then admitted from a water tube similar to those used for supplying water during the adsorption measurements The adsorption bulb was evacuated again until the silk was perfectly dry, the residual traces of air being removed with water vapour.

The samples examined consisted of white Japanese, white Chinese, and yellow Italian silks in the form of raw filature silk. Investigations were made on the material in the gum state, as received, and also after degumming according to the following procedure:—The silk was immersed in a 1 per cent. solution of textile soap flakes for one hour at 95-100° C. It was centrifuged, given two washes in a large bulk of water at about 40-50° C., again centrifuged, and allowed to dry at room temperature. A sample of the degummed Japanese silk was made iso-electric by immersing it for 24 hours in 0·02N-acetic acid and then washing repeatedly in distilled water until the *pH* of the wash water was unchanged by contact with the silk.

Speakman[17] has suggested that in the vacuum method as used for these experiments the conditions are not such as will give true adsorption and desorption. Adsorption takes place under a continuously diminishing pressure and at some stage in the process parts of the adsorbent will adsorb more water than corresponds with the final pressure of water vapour and these parts of the material must subsequently lose water to that which was less accessible so that the amount of water in one part of the adsorbent will correspond with a desorption process whilst that in the other will correspond with true adsorption. Similar observations are applicable to the removal of water from a closed vessel containing the absorbent so that there is a possibility that the magnitude of the hysteresis between the adsorption and desorption curves will be reduced.

It was obviously desirable to ascertain whether the results obtained by the vacuum method differed significantly from those obtained when adsorption and desorption are carried out at constant partial pressure of water vapour, and additional measurements of the regain of the degummed Japanese silk were therefore made by exposing samples, in evacuated desiccators, to atmospheres in equilibrium with sulphuric acid solutions of known concentration. In these experiments 1½-2 grams of the sample were placed in each of five weighing bottles. The samples were dried to constant weight in a vacuum desiccator over phosphorus pentoxide at room temperature The phosphorus pentoxide was then replaced by a sulphuric acid solution of a concentration sufficient to give the required humidity and the desiccators were placed in an air thermostat at 25° C The bottles were removed from the desiccator for weighing at intervals until no further directional change in weight took place. When equilibrium had been attained the concentration of the sulphuric acid was determined by means of a pyknometer and the corresponding humidity was calculated from Wilson's data.[18] The adsorption regains at relative humidities of 20, 40, 60, 80, 90 and 95 per cent. were determined in this way, after which the acid solution was replaced by water and the samples were exposed for sufficient time for saturation to be attained. The desorption regains were then found in a similar manner by using sulphuric acid solutions of increasing concentration and the dry weight was finally checked by drying over phosphorus pentoxide again.

III. EXPERIMENTAL RESULTS

Vacuum Method

The corresponding values of regain and relative humidity obtained for the various silks are given in Tables I and II. The adsorption-desorption cycle was usually traversed more than once although measurements were not necessarily made during both adsorption and desorption in every cycle; the results obtained in the different cycles are in very good agreement. These results were plotted on a large scale and a smooth curve was drawn through the points for each sample, a typical isotherm so obtained being shown in Fig. 1. It was not practicable to reproduce all the isotherms in one figure and as the data of Tables I and II are not in a suitable form to enable a direct comparison to be made between the various samples, Table III has been constructed from the smoothed curves giving values of the regain for all the silks at selected relative humidities

Table I. Silk in the Gum

CHINESE				JAPANESE				ITALIAN			
Adsorption		Desorption		Adsorption		Desorption		Adsorption		Desorption	
% R H	% Regain	% R H	% Regain	% R H	% Regain	% R.H.	% Regain	% R H.	% Regain	% R.H.	% Regain
1st Cycle		1st Cycle		1st Cycle		1st Cycle		1st Cycle		1st Cycle	
0·3	0·43	99·4	36·74	0·3	0·26	98.5	34·49	1·8	1·37	97·4	31·37
1·0	0·98	98·7	34·11	1·2	1·02	97·8	32·08	7·2	2·77	95·7	27·27
3·4	1·61	96·6	28·41	4·8	2·19	97·0	29·71	13·1	3·81	91·8	22·51
8·5	2·81	95·2	26·02	24·8	5·40	95·7	26·74	20·9	4·93	80·7	15·98
16·2	4·07	73·7	13·80	42·2	7·67	90·0	20·64	28·7	6·02	69·1	13·13
25·7	5·43	49·0	10·01	64·2	10·63	81·5	16·16	42·7	7·88	50·5	10·32
35·3	6·67	25·6	7·08	77·7	13·25	75·1	13·83	59·0	10·19	32·1	8·01
54·2	9·09	11·8	4·98	90·9	18·99	61·4	11·51	72·3	12·48	12·2	4·86
62·2	10·12	5·0	3·57	94·5	22·66	45·0	9·51	84·3	16·14	5·0	3·37
68·5	11·34	0·5	0·71	96·6	26·05	28·8	7·28	90·8	19·97	1·7	1·99
74·9	12·58	2nd Cycle		98·2	29·36	11·9	5·05	95·0	23·45		
79·1	13·72	97·5	31·05	99·3	32·75	8·5	4·21	97·0	26·92		
82·9	14·92	96·6	28·37	100·0*	40·62	2·3	1·97	98·5	31·79		
85·8	16·22	95·5	26·85	2nd Cycle		2nd Cycle		99·4	34·70		
92·1	20·02	93·9	23·58	0·3	0·29	98·6	32·75	100·0*	41·91		
93·8	21·89	91·6	21·27	2·1	1·30	96·6	28·49	2nd Cycle			
95·6	23·92	86·2	18·17	6·2	2·39	93·9	24·25	2·2	1·45		
97·0	26·20	79·8	15·57	73·6	12·22	39·7	8·67	8·7	3·02		
98·6	30·67	66·3	12·52	89·1	17·88	23·3	6·48	19·3	4·66		
99·6	33·43	48·8	9·85	95·4	23·57	4·8	3·37	30·6	6·27		
99·8	35·19	3rd Cycle		98·1	29·24	1·3	1·34	45·4	8·15		
100·0*	36·04	98·7	33·62	99·6	33·95	3rd Cycle		72·9	12·56		
2nd Cycle		97·4	30·26	99·8	36·32	99·6	36·81	97·9	29·83		
0·2	0·23	95·9	26·69	100·0*	39·47	97·6	30·18	98·3	31·26		
2·1	1·34	93·1	22·63			96·0	26·94	98·9	33·62		
8·8	2·82	74·5	13·74			93·9	23·43	99·9	38·02		
29·0	5·79	55·3	10·62			88·2	18·72	100·0*	39·97		
71·5	11·80	13·6	5·14			82·7	16·12	3rd Cycle			
88·1	17·41	4·8	3·17			56·4	10·76	0·5	0·59		
94·8	23·22	1·5	1·87			38·2	8·61	55·8	9·79		
96·9	26·71	0·5	1·01			21·7	6·48	71·9	12·33		
98·5	30·58					10·5	4·60	82·0	15·19		
99·7	34·94					4·6	3·12	90·2	19·54		
100·0*	37·41					1·3	1·68	97·4	28·89		
								100·0*	41·53		

* Condensed water in adsorption bulb

Table II. Degummed Silk

CHINESE				JAPANESE				ITALIAN				JAPANESE ISO-ELECTRIC	
Adsorption		Desorption		Adsorption		Desorption		Adsorption		Desorption		Adsorption	
% R H	% Regain	% R H	% Regain	% R H	% Regain	% R H.	% Regain	% R H	% Regain	% R H	% Regain	% R H	% Regain
1st Cycle		1st Cycle		1st Cycle		1st Cycle		1st Cycle		1st Cycle		1st Cycle	
0·4	0·48	98·7	35·74	0·1	0·17	99·6	39·65	2·1	1·21	98·6	34·67	0·1	0·19
2·1	1·21	97·8	31·27	2·1	1·27	98·7	35·46	17·1	4·01	97·6	30·48	1·6	0·91
5·9	2·11	95·9	26·78	6·9	2·36	98·1	32·40	37·4	6·53	92·8	22·38	7·2	2·24
10·3	2·87	92·8	21·99	15·6	3·74	96·7	28·73	57·9	9·07	87·5	18·08	14·9	3·65
16·1	3·77	88·0	18·40	30·4	5·55	94·6	24·49	72·8	11·53	81·0	14·83	25·8	4·75
32·1	5·60	82·0	15·21	45·4	7·29	92·1	21·65	81·5	13·96	71·7	12·45	71·3	10·72
42·1	6·81	60·2	10·40	68·8	10·53	89·8	19·45	88·1	17·03	60·3	10·59	81·1	12·94
52·2	8·06	42·1	7·94	81·8	13·87	86·1	17·16	93·5	21·26	33·4	7·27	2nd Cycle	
60·9	9·28	18·4	5·15	90·2	18·31	82·2	15·45	98·5	30·42	26·5	6·33	3·4	1·41
68·1	10·42	5·2	2·86	95·8	24·00	61·2	10·38	100·0*	38·41	17·5	5·24	9·2	2·82
74·3	11·64	1·4	1·42	98·1	28·62	45·7	8·43	2nd Cycle		12·7	4·40	21·1	4·23
79·4	13·10	0·5	0·49	99·4	32·89	31·1	6·71	2·1	1·10	9·9	4·03	32·8	5·64
83·6	14·49	2nd Cycle		100·0*	36·59	16·4	4·89	6·6	2·20	5·1	3·01	43·9	6·97
87·5	16·27	99·1	34·50			5·2	2·85	17·4	3·98	2·6	1·91	60·0	8·96
90·5	18·27	98·1	31·55			2·5	1·91	29·7	5·45	2nd Cycle		69·5	10·37
94·0	21·72	94·4	24·26			0·5	0·49	50·5	8·09	97·8	32·40	77·1	11·92
96·0	24·34	90·6	20·26					66·9	10·40	94·8	25·46	3rd Cycle	
97·5	27·28	86·0	17·19					77·8	12·86	92·1	22·34	0·5	0·46
98·8	30·95	73·4	12·55					89·6	17·78	78·2	14·28	5·8	2·06
99·9	35·74	54·8	9·61					96·1	24·53	57·4	10·23	28·0	5·19
100·0*	38·29	21·2	5·65					99·0	32·51	47·4	8·82	61·8	9·31
2nd Cycle		9·8	3·89					99·9	36·16	30·9	7·04	4th Cycle	
10·5	2·85	2·0	1·65					100·0*	38·61	18·0	5·36	0·3	0·33
19·4	4·08	1·1	0·90							8·8	3·75	3·0	1·44
35·6	6·03	3rd Cycle								3·2	2·21	24·4	4·77
45·8	7·27	99·6	36·31							0·8	0·88	64·1	9·59
58·4	9·05	98·2	32·15										
74·5	11·80	96·8	27·97										
94·2	21·90	93·9	23·41										
97·4	27·12	74·3	12·74										
99·3	32·13	51·8	9·15										
99·7	33·67	26·0	6·08										
100·0*	37·90	7·6	3·32										
		2·3	1·68										
		1·0	0·80										

* Condensed water in adsorption bulb.

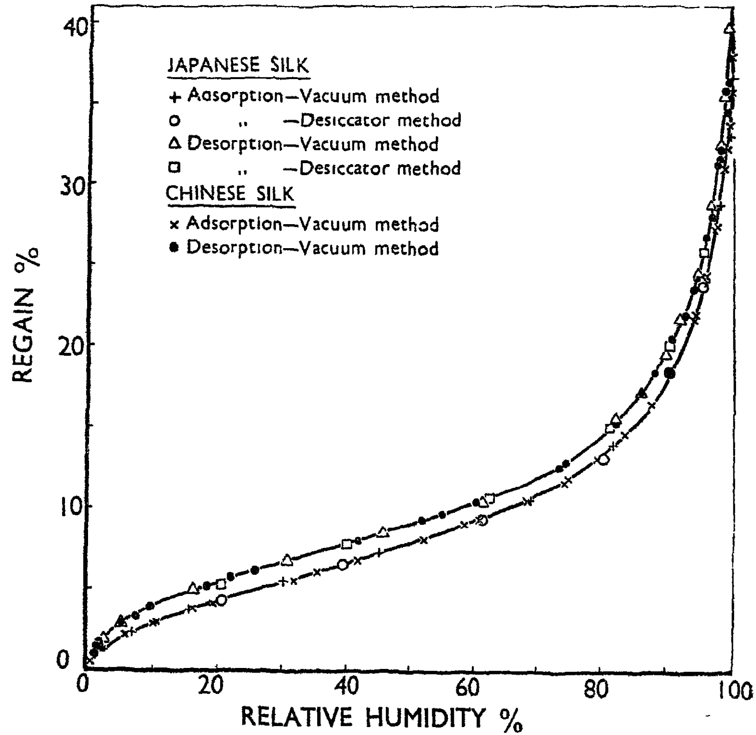

Fig. 1. Degummed Japanese and Chinese Silks

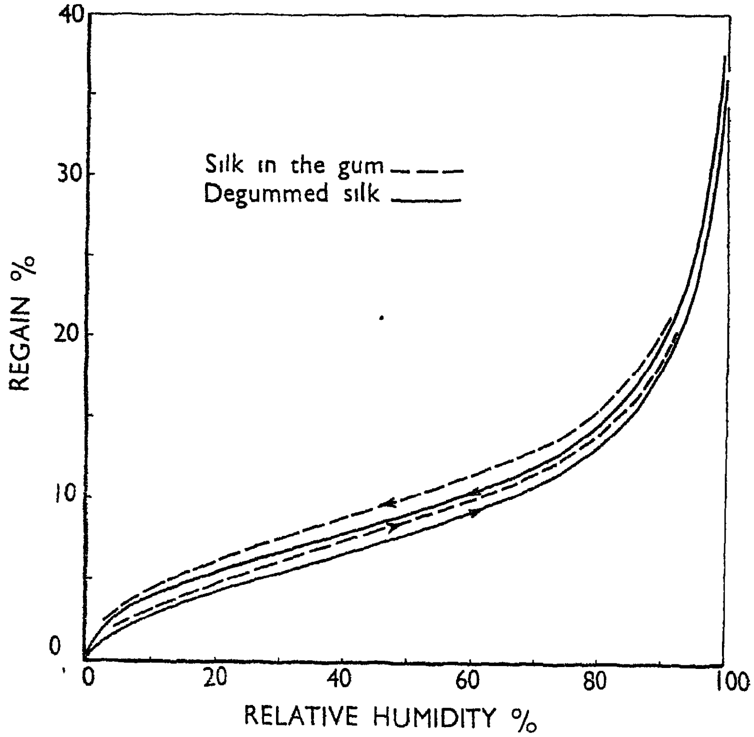

Fig. 2. Japanese and Chinese Silks before and after Degumming.

Identical isotherms were obtained for the Japanese and Chinese silks, both in the gum and again after degumming. This is shown for the degummed material by Fig. 1 In Fig 2 are reproduced, for comparison, the common isotherms for these two silks before and after degumming; the regains are greater at all humidities for the silk in the gum than for the degummed silk. A similar set of curves was given by the Italian silk which was slightly more hygroscopic than the Japanese and Chinese silks although the difference for degummed silk is very small and is probably not significant

Table III. Regain, %

	Silk in the gum				Degummed silk				
	Japanese and Chinese		Italian		Japanese and Chinese		Italian		Iso-electric Japanese
% R H	Adsorption	Desorption	Adsorption	Desorption	Adsorption	Desorption	Adsorption	Desorption	Adsorption
5	2 15	3 30	2 25	3 35	1 95	2 85	1 95	2 85	1 90
10	3·10	4 55	3 30	4 70	2 90	3 95	2 95	4 00	2 85
20	4 60	6·10	4 80	6 35	4 20	5 40	4 35	5 50	4·20
30	6 00	7 50	6 20	7 70	5 40	6 65	5 55	6·80	5 35
40	7 30	8 75	7 55	9 05	6 60	7 80	6 75	7 95	6 50
50	8 60	10 05	8·90	10 30	7·80	9 00	8 00	9·15	7 65
60	9 90	11·35	10 25	11 65	9 15	10 30	9 30	10 50	8 95
65	10 65	12 15	11 00	12 45	9 90	11·05	10 10	11 25	9 65
70	11 50	13 00	11 90	13 30	10 75	11·90	10 95	12 10	10·50
80	13·95	15 50	14 45	15 80	13·30	14·50	13 50	14 70	12·65
90	18 50	20 40	19 20	20 90	18 10	19 80	18 30	20 00	—
95	23 20	25 50	24 00	26 30	22 90	25·20	23 10	25 40	—
100	Approx 37	—	Approx 39	—	Approx 36	—	Approx 37	—	—

All the samples show a considerable hysteresis between the adsorption and desorption regains, the difference at 65 per cent. R.H. being approximately 1 50 per cent for the gum silk and 1 15 per cent. for the degummed material.

The adsorption isotherm for degummed Japanese and Chinese silks cuts the ordinate corresponding to 100 per cent. R.H at a regain value very close to 36 per cent , Goodings and Turl[14] give a value of 35 8 per cent. for the saturation regain of degummed and purified Japanese silk as deduced from density and swelling data.

The results for the iso-electric sample of the degummed Japanese silk are incomplete. Several attempts were made to determine the moisture uptake of this material but although excellent agreement was shown between the results of the different experiments during adsorption between 0 and about 80 per cent. R.H., large discrepancies were obtained at higher humidities and the pressure obtaining in the manometer at saturation was frequently greater than the saturation pressure of water vapour. It is known that silk in the iso-electric state is less stable than when it contains traces of alkali such as remain following the normal degumming procedure and the conclusion was drawn that during the course of the experiments degradation of the iso-electric silk occurred, this degradation being accelerated in atmospheres of high humidity. In view of the reproducibility of the results below about 80 per cent. R H. it may be assumed that in this region errors due to possible degradation of the silk are small. The adsorptive capacity of degummed Japanese silk appears to be slightly reduced when the silk is made iso-electric by the treatment previously described.

Desiccator Method

Only two samples were examined by the desiccator method, namely the ordinary degummed and the iso-electric Japanese silks. The results are given in Table IV together with the corresponding values obtained by the vacuum method for comparison, the latter being read off from the smoothed isotherms The results obtained by the desiccator method for the ordinary degummed silk are also indicated in Fig. 1. No desorption regains are given for the iso-electric silk, the validity of the determined values being questionable owing to the probable degradation of the silk during the later stages of the adsorption measurements

Table IV

Degummed Japanese silk						Iso-electric degummed Japanese silk		
	Adsorption regain %			Desorption regain %			Adsorption regain %	
R H %	Desiccator method	Vacuum method	R H %	Desiccator method	Vacuum method	R H %	Desiccator method	Vacuum method
20 7	4·28	4 30	95 2	25 81	25·40	20 7	4·17	4 30
39 7	6 42	6 55	90 2	20 09	19 90	39 7	6 32	6 45
60·7	9 28	9 25	81·2	14 94	14 90	60 7	9·16	9 05
80·2	13 03	13·30	62 3	10 62	10 65	80 2	12 77	12 70
90·5	18 35	18 50	40 2	7 71	7 80	90 5	17 92	—
95 2	23·63	23 20	20 7	5 27	5 50			

The results obtained by the two methods agree very well and it is apparent that any errors that may be introduced into the regain values given by the vacuum apparatus, owing to the fact that adsorption and desorption do not take place at constant pressure of water vapour, are of negligible magnitude.

Regain of Sericin

It has been shown that the regain of silk in the gum is always greater than that of degummed silk under similar conditions and that the adsorption and desorption isotherms for gum silk are further apart than for the degummed material. It is therefore clear that silk gum, or sericin, has not only a greater adsorptive capacity for water vapour than has fibroin but also shows a greater degree of hysteresis. From a knowledge of the gum contents of the silks examined, it is possible to calculate values for the moisture regain of the sericin although these values are necessarily less accurate than those for the fibroin since they are obtained by difference and are based on a smaller weight of material. The results obtained, calculated from the data of Table III, are shown in Table V In this calculation of the regain of sericin, it has been assumed that the adsorptive capacity of the fibroin was unaltered by the degumming process. Recent experiments, still in progress, indicate that the regain of fibroin is dependent to some extent on the degree of its acidity or alkalinity and this assumption may not, therefore, be strictly correct It is unlikely that the acidity or alkalinity of the silk degummed by the method described will differ to any great extent from that of the original silk in the gum, but the possibility of additional error from this source cannot be ignored. In view of the approximate nature of the values in Table V no significance can at this stage be attached to the different regains shown for the gum of the Italian silk and that of the Japanese and Chinese silks

The gum contents of the Japanese, Chinese and Italian silks, determined on the actual samples used for the regain measurements, were found to be 20·1, 20 6 and 24 8 per cent , respectively For the purpose of calculation, these have been rounded off to 20 per cent. for the Japanese and Chinese silks and 25 per cent for the Italian silk

Table V. Regain of Sericin, per cent.

	Adsorption		Desorption	
R H %	Japanese and Chinese	Italian	Japanese and Chinese	Italian
5	2·95	3·15	5·10	4·85
10	3·90	4·35	6·95	6·80
20	6·20	6·15	8·90	8·90
30	8·40	8·15	10·90	10·40
40	10·10	9·95	12·55	12·35
50	11·80	11·60	14·25	13·75
60	12·90	13·10	15·55	15·10
70	14·50	14·75	17·40	16·90
80	16·55	17·30	19·50	19·10
90	20·10	21·90	22·80	23·60

SUMMARY

The adsorption and desorption isotherms at 25° C have been determined for Japanese, Chinese, and Italian silks, both in the gum and after degumming.

The degummed silks have a lower regain than the corresponding silks in the gum at all humidities and also show less hysteresis between the adsorption and desorption isotherms

When degummed, the different kinds of silk adsorb water to the same, or nearly the same, extent but in the gum state the adsorption is greater for the Italian silk than for the Japanese and Chinese silks.

Slightly lower values were found for the regain of "iso-electric" degummed Japanese silk than for the same silk before treatment.

Approximate values for the regain of sericin have been deduced.

REFERENCES

[1] Muller *Dinglers Polytech J*, 1882, 245, 210, *J Soc Chem Ind*, 1882, 1, 356.
[2] Schloesing. *C r Acad Sci, Paris*, 1893, 116, 808
[3] Scheurer *Bull Soc Ind Mulhouse*, 1900, 70, 89, 1921, 87, 129
[4] Levrat *Rapp Lab Soie, Lyon*, 1899-1900, 10 39
[5] Kujirai, Kabayashi, and Toriyama *Sci Papers Inst Phys Chem Res, Tokyo*, 1923, 1, 79
[6] Honig, *Forschungsheft dtsch Forsch Inst Textilind*, 1918, No 3-5, 98
[7] Obermiller and Goertz *Textilberichte*, 1926, 7, 71
[8] McBain, " The Sorption of Gases and Vapours by Solids," p 382 (London, 1932)
[9] Denham and Allen *Trans Faraday Soc*, 1933, 29, 316
[10] Schaposchnikov *Sbornik Inst Akad. Nauk, U S S R.*, 1937, No 3, 119 (through *Chem Zentr*, 1938, 1, 471)
[11] Oguri *J Soc Chem Ind Japan*, 1932, 35, 478B
[12] Carr *Textile Research*, 1940, 10, 126
[13] Wiegerink *Textile Research*, 1940, 10, 357, *J Res Nat Bur Stnds*, 1940, 24, 645
[14] Goodings and Turl *J Text Inst*, 1940, 31, T69
[15] Bull *J Amer Chem Soc*, 1944, 66, 1499
[16] Urquhart and Williams *Shirley Inst Mem*, 1924, 3, 197, or *J Text Inst*, 1924, 15, T433
[17] Speakman, *J Soc Chem Ind*, 1930, 49, 209 T
[18] Wilson *J Ind Eng Chem*, 1921, 13, 326

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8—THE ADSORPTION AND DESORPTION OF WATER BY NYLON AT 25°C.

By E. A. HUTTON and JOAN GARTSIDE

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I. INTRODUCTION

Results for the moisture regain of nylon yarn at various relative humidities have been given by the nylon division of Messrs. E. I. du Pont de Nemours & Co., Inc.[1] and by Loasby.[2] Bull[3] has included nylon in a study of the adsorption of water vapour by proteins and gives regain values for drawn and undrawn nylon at temperatures of 25° C. and 40° C. None of these reports states whether the experiments were carried out under adsorption or desorption conditions.

A more detailed examination of the moisture relations of nylon has been made by Speakman and Saville[4] who have determined the adsorption and desorption isotherms of bright and delustred nylon yarn and also undrawn nylon.

The investigation here described was mostly carried out before the last-mentioned paper was published and the values of regain found are, in general, in good agreement with those given there for drawn nylon, except at very high humidities. There is, however, an important difference between the two sets of results. Whereas Speakman and Saville found no evidence of hysteresis between the adsorption and desorption isotherms such as generally occurs with textile fibres, the present experiments, in which two entirely different methods were used, show a small but definite separation between the two curves

It should be noted that the results refer to the nylon in common use as a textile fibre at the present time, i.e the condensation product of hexamethylenediamine and adipic acid, sometimes designated "66" nylon. This is important since nylon is a generic term for all synthetic fibre-forming polyamides and it is likely that special polyamides will be developed later for various purposes.

II. EXPERIMENTAL METHODS

Both the vacuum and desiccator methods were used for the investigation as described in the preceding paper on the Moisture Regain of Silk.

The material used consisted of a parachute fabric woven from delustred yarn supplied by Messrs. British Nylon Spinners Ltd After weaving, this fabric was scoured in a solution containing 0·5 per cent. of soap and 0·01 per cent. of caustic soda at 90° C. for one hour, after which it was well washed in hot water (50-60° C.) and dried on steam-heated cylinders The fabric was then allowed to condition under normal atmospheric conditions

For the desiccator experiments, this material was dried over phosphorus pentoxide at room temperature without further treatment but in the vacuum experiments the nylon was dried by evacuating the sample tube, then saturated with air-free distilled water to displace the remaining traces of air from the sample, and again dried by evacuation.

III. EXPERIMENTAL RESULTS

Vacuum Method

For the determinations made with the vacuum apparatus the complete adsorption-desorption cycle was traversed three times. The results for the three cycles, which are in good agreement, are given in Table I, the corresponding isotherms being shown in Fig I.

The desorption regain is always higher than the adsorption regain at the same relative humidity but the area enclosed by the adsorption and desorption curves is very small compared with that shown by most other fibres.

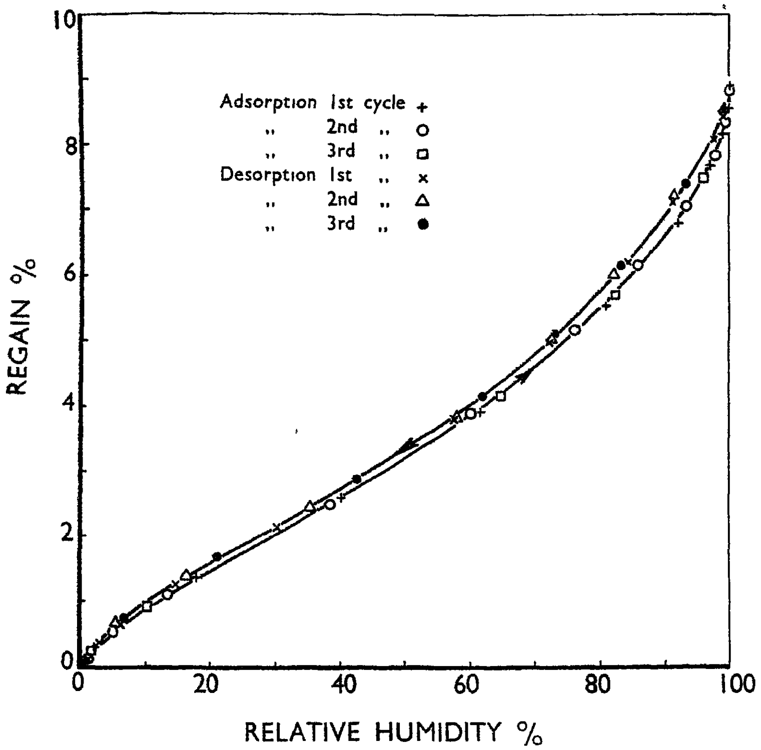

Fig. 1. Vacuum Method.

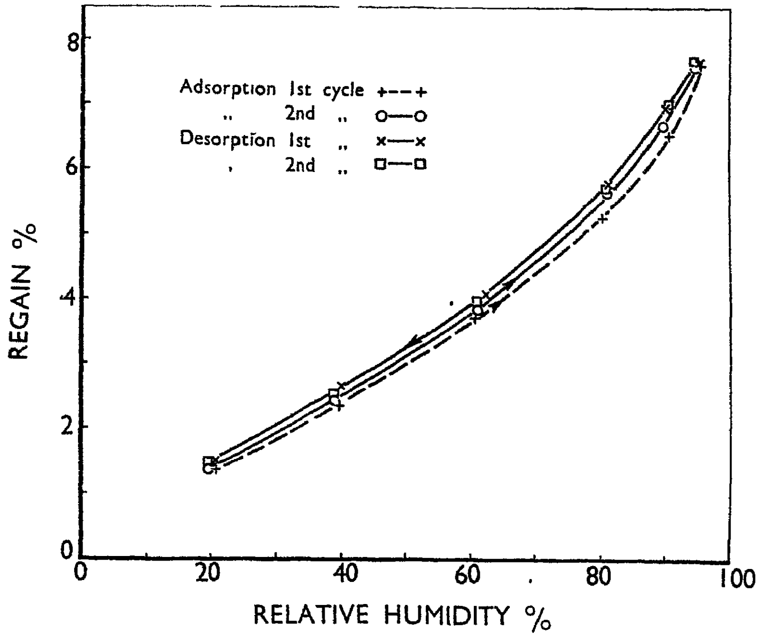

Fig. 2. Desiccator Method.

The regain at saturation lies between 8·53 per cent and 8·79 per cent and is probably about 8·70 per cent.

Table I

Adsorption						Desorption					
1st cycle		2nd cycle		3rd cycle		1st cycle		2nd cycle		3rd cycle	
% R H	% Regain	% R H	% Regain	% R H	% Regain	% R H	% Regain	% R H	% Regain	% R H	% Regain
0·5	0·08	1·0	0·12	1·8	0·23	99·2	8·40	99·3	8·51	99·2	8·52
2·5	0·34	4·8	0·52	10·2	0·92	97·8	8·06	91·7	7·22	93·5	7·38
17·9	1·36	13·4	1·08	65·0	4·13	91·4	7·09	82·3	5·99	83·3	6·13
40·2	2·59	38·5	2·49	82·6	5·69	84·3	6·16	72·8	4·99	73·2	5·07
61·6	3·89	60·1	3·85	96·1	7·46	72·4	4·94	58·0	3·76	62·0	4·13
81·1	5·51	76·1	5·14	100·0*	9·38	57·9	3·76	35·6	2·44	42·7	2·86
92·2	6·77	85·9	6·14			42·7	2·80	16·4	1·38	21·0	1·68
97·3	7·65	93·3	7·05			30·4	2·12	5·3	0·67	6·5	0·74
99·0	8·15	98·0	7·82			14·9	1·26	1·1	0·12	0·5	0·07
99·9	8·53	99·5	8·33			6·1	0·64				
100·0*	8·87	100·0*	8·79			2·8	0·38				
						1·1	0·13				

* Condensed water in adsorption bulb

Desiccator Method

The regain values obtained by the desiccator method are given in Table II. Four samples of nylon, each of 1·5—2 grams in weight, were used for the first adsorption-desorption cycle. At the end of this cycle, two of the samples were accidentally contaminated with acid and had to be rejected but a second cycle was carried out on the two remaining samples supplemented by four additional samples taken from the material previously used in the vacuum apparatus. In Table II (2nd Cycle), the values in the column headed (i) are the average for the two original samples from the 1st cycle and those in the column headed (ii) are the average for the four new samples, no significant difference is apparent between the results in columns (i) and (ii). The mean values refer to all six samples and have been used when plotting the isotherms shown in Fig. 2.

Table II

1st Cycle

Adsorption		Desorption	
% R H	% Regain	% R H	% Regain
20·7	1·38	95·2	7·65
39·7	2·38	90·2	6·96
60·7	3·72	81·2	5·78
80·2	5·25	62·3	4·06
90·5	6·55	40·2	2·63
95·2	7·59	20·7	1·50

2nd Cycle

Adsorption				Desorption			
% R H	% Regain			% R H	% Regain		
	(i)	(ii)	Mean		(i)	(ii)	Mean
19·7	1·37	1·36	1·36	94·4	7·70	7·66	7·67
38·8	2·42	2·44	2·43	90·3	7·01	7·00	7·00
61·0	3·83	3·85	3·84	80·7	5·69	5·74	5·72
80·7	5·61	5·66	5·65	60·7	3·93	3·98	3·96
89·5	6·66	6·68	6·67	39·0	2·50	2·55	2·53
94·6	7·64	7·55	7·58	19·7	1·47	1·52	1·50

It will be noticed that although the desorption regains in the 1st and 2nd cycles lie on the same curve the adsorption regains are distinctly higher for the second cycle than the first. An explanation of the lower adsorption values obtained in the 1st cycle is to be found in the previous history of the material and is referred to later. Although no further cycles were traversed in these desiccator experiments, it is safe to assume that if these had been carried out the results would have agreed with those obtained in the second cycle, since the values in column (ii) of Table II, which are for material that had already been through three cycles in the vacuum apparatus, are essentially the same as those in column (i).

The results obtained in the desiccator experiments (2nd cycle) are in good agreement with those given by the vacuum method and hysteresis between the adsorption and desorption curves is again shown.

Since these experiments were completed, a paper has been published by Speakman and Saville (*loc. cit.*) describing experiments that fail to show any such hysteresis and it was therefore thought advisable to make a further check on this point. Two samples of nylon dried over phosphorus pentoxide at room temperature and two samples which had been exposed to water vapour in a closed desiccator for about a week were placed together in an evacuated desiccator over a sulphuric acid solution adjusted to give a relative humidity of 80 per cent. at 25° C. An additional set of samples similar to the above except that the nylon was initially purified by extraction with alcohol and ether followed by washing in distilled water was included in the same desiccator. The samples were weighed periodically until no directional change in weight was observed after which twelve further weighings on each sample were made at intervals during a period of six weeks. The regains of the samples calculated from the mean of the twelve weights are shown in Table III and confirm the existence of hysteresis.

Table III

Extracted nylon:	adsorption regain, %	5·48,	5·51
	desorption regain, %	5·64,	5·63
Unextracted nylon:	adsorption regain, %	5 63,	5 58
	desorption regain, %	5·70,	5·71

It has been noted that the adsorption regains obtained in the first cycle of the desiccator experiments are lower than those obtained in the second cycle. The only difference between the experimental conditions in the two cycles lies in the initial condition of the nylon. After scouring, the nylon fabric was dried on steam-heated cylinders. This material was stored under atmospheric conditions and was then simply dried over phosphorus pentoxide at room temperature at the start of the experiments, whereas in the second cycle and also in the experiments by the vacuum method the nylon had been saturated with water at either room temperature or 25° C. previous to drying. It is known that the absorptive capacity of cotton,[5] wool,[6] and jute[7] is reduced by drying or partial drying at a high temperature and Speakman and Stott[6] have further demonstrated that a normal affinity for water may be restored to wool that has been dried at a high temperature by allowing it to reach saturation with water vapour. It appeared worth while to ascertain whether a similar behaviour was shown by nylon.

Four samples of nylon were allowed to come to approximate equilibrium with an atmosphere of 80 per cent. R H. Two of the samples were then heated for 12 hours at a temperature of 85-90° C. and the other two were heated for 4½ hours at 110° C. A comparison of their weights with their known dry weights showed that they were very nearly dry but they were brought to absolute dryness by leaving in an evacuated desiccator over phosphorus pentoxide at room temperature until constant in weight. The phosphorus pentoxide was replaced by a suitable sulphuric acid solution and the adsorption regain of the samples was determined at 80 per cent. R.H and 25° C. The samples were then saturated by leaving over water in an evacuated desiccator for about a week and were again placed over the sulphuric acid solution to determine the desorption regains at 80 per cent R.H and 25° C After drying over phosphorus pentoxide, the adsorption regain at the same humidity was re-determined The results are given in Table IV.

Table IV

	Dried for 12 hours at 85-90°C		Dried for 4½ hours at 110°C	
Adsorption regain, %	5 40	5 39	5 10	5 06
Desorption regain, %	5 72	5 75	5 57	5 50
2nd adsorption regain %	5 62	5 63	5 51	5 45

On comparing these values with those in Table III for unextracted nylon dried at room temperature, it is seen that (*a*) the adsorptive capacity of nylon decreases with increasing temperature of drying and (*b*) on saturation with water, the effect of the heating is either wholly or partially removed according to the temperature of drying, so that the desorption regain and subsequent adsorption regain are similar to, or only a little less than, those of the unheated material The combined effect of (*a*) and (*b*) is that the hysteresis between the adsorption and desorption regains is increased when the nylon is dried at a high temperature

The foregoing results appear to provide an adequate explanation of the low adsorption values obtained during the first cycle in the determination of the regain curve since it may be assumed that the adsorptive capacity of the nylon was reduced by the drying on the steam-heated cylinders during the finishing of the fabric The normal affinity for water would be restored by saturation with water vapour

SUMMARY

The adsorption and desorption isotherms for nylon have been determined at 25° C ; the curves show a small, but definite hysteresis

A value of approximately 8 70 per cent has been found for the regain at saturation

The adsorptive capacity of nylon decreases with increasing temperature of drying but subsequent saturation with water vapour restores the normal affinity for water either completely or to a large extent, depending on the drying temperature

REFERENCES

[1] E I du Pont de Nemours & Co , Inc *Amer Dyestuff Rep* , 1930, 28, 198 , *Text. Manufacturer*, 1939, 65, 222 , *Silk Journal*, 1939, 16, June, p 15
[2] Loasby *J Text Inst*, 1943, 34, P45
[3] Bull *J Amer Chem Soc* , 1944, 66, 1499
[4] Speakman and Saville *J Text Inst* , 1946, 37, P271
[5] Urquhart and Williams *Shirley Inst Mem* , 1924, 3, 49 , or *J Text Inst* , 1924, 15, T138
[6] Speakman and Stott *J Text Inst* , 1936, 27, T186
[7] Macmillan, Mukherjee, and Sen *J Text Inst* , 1946, 35, T13

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9—THE EFFECT OF THE CARBOXYL GROUPS IN VISCOSE SHEET ON THE EQUILIBRIUM ABSORPTION OF CHRYSOPHENINE G.

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The equilibrium absorption of Chrysophenine G on viscose sheet was found to depend on the ratio of the mass of sheet to the volume of the dyebath. This effect, which was greatest when the concentration of sodium chloride in the dyebath was low, was due to the presence in the viscose sheet of acidic carboxyl groups which resulted in a lowering of the dyebath *pH*. For dyebaths in which the dye concentration and the total cation concentration of the inorganic electrolytes were maintained constant, the equilibrium absorption increased with decreasing dyebath *pH* and attained a fairly constant value at *pH*s between 3 and 2. The absorption isotherms of Chrysophenine on viscose sheet were measured under conditions such that the dyebath *pH*s were about 6.

The theory of the effect of carboxyl groups in viscose sheet on the equilibrium absorption is discussed. Tentative calculations based on this theory suggest that the number of carboxyl ions which directly affect the equilibrium absorption may be less than the total number of carboxyl groups in the viscose sheet.

A study of the equilibrium absorption of the direct dye Chrysophenine G on viscose sheet has been described in an earlier paper,[1] and a study of the diffusion of this dye in viscose sheet will be described in a later paper. Although commercial Cellophane was a convenient source of viscose sheet for the equilibrium absorption measurements, a more highly swollen viscose was convenient for the diffusion measurements, and viscose sheet that had never been allowed to dry was therefore used. This material, which has a much higher water imbibition than Cellophane, will be called never-dry sheet. Since equilibrium absorption measurements were required for the interpretation of the diffusion data, the absorption isotherms of Chrysophenine G on the never-dry sheet were measured. The results so obtained are described separately in this paper because they show that the presence of carboxyl groups in the viscose sheet affects the absorption of Chrysophenine, and that any theory of the direct dyeing of viscose sheet must take into account the fact that it is an acidic oxycellulose.

When the never-dry sheet was dyed to equilibrium with Chrysophenine in solutions containing sodium chloride of low concentration, the equilibrium absorption was found to depend on the ratio of the mass of viscose sheet to the volume of the dye solution. This quantity will be called the "relative mass" of viscose sheet, and will be expressed as grams of viscose sheet per 100 ml. of solution. Fig. 1 shows the isotherms obtained at 90° C. for never-dry viscose sheet in equilibrium with Chrysophenine solutions containing 0·5 g. of sodium chloride per litre when the relative mass of viscose sheet was (*a*) 0·015 g./100 ml., (*b*) 0·52 g./100 ml. It shows that for a given concentration of dye in solution, the equilibrium absorption is greater when the relative mass is high than when it is low. Fig. 2 shows the isotherms obtained at 90° C. when the concentration of sodium chloride in solution was 10 g./l., the relative masses of viscose sheet being again 0·015 g. and 0·52 g. per 100 ml. With this high concentration of sodium chloride in solution, the isotherm is not significantly affected by the large difference in the relative mass of viscose sheet.

It was observed that the *pH* of the equilibrium solution also varied with the relative mass of viscose sheet. The introduction of viscose sheet into an unbuffered dye solution containing sodium chloride resulted in a fall in the *pH* of the solution, which was greater the greater the relative mass of sheet.

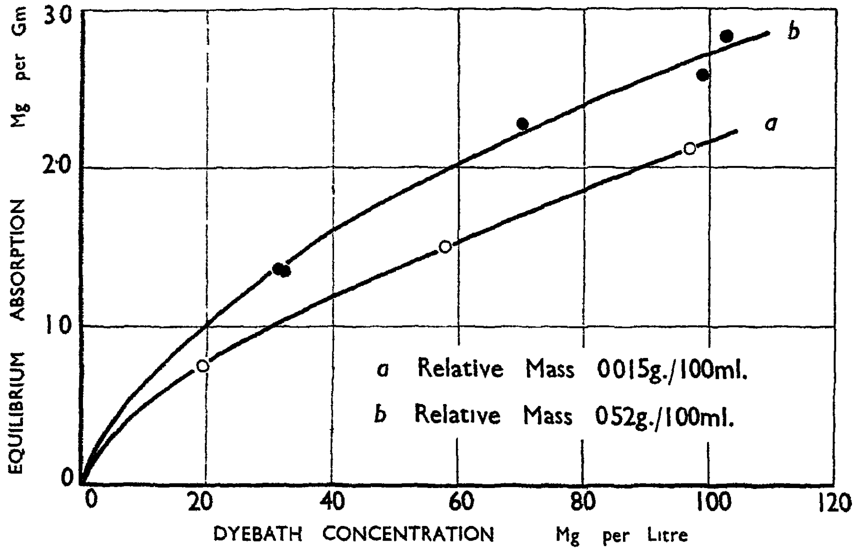

Fig. 1.

Absorption isotherms of Chrysophenine G on never-dry viscose sheet at 90°C Unbuffered dyebaths containing 0·5 gm. sodium chloride per litre and different relative masses of sheet

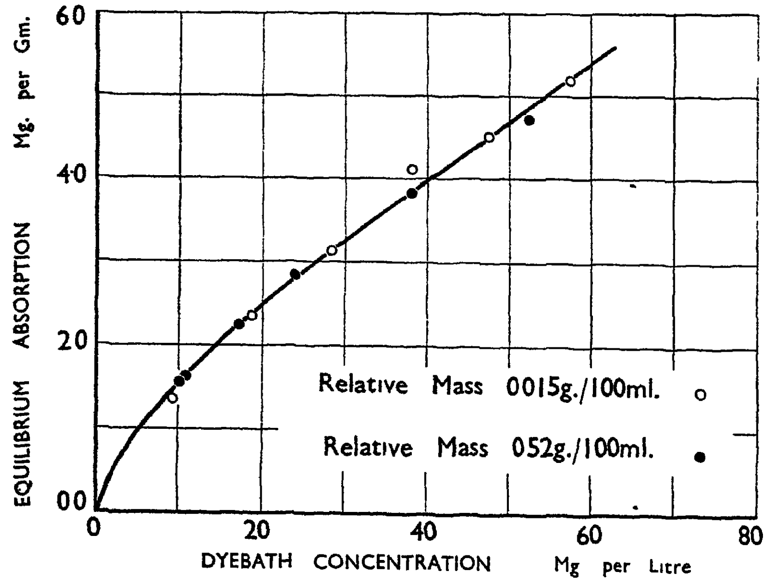

Fig. 2.

Absorption isotherms of Chrysophenine G on never-dry viscose sheet at 90°C Unbuffered dyebaths containing 10 gm sodium chloride per litre and different relative masses of sheet

Thus when the relative mass was as small as 0·015 g./100 ml., the *p*Hs of the equilibrium solutions were between 6 and 6·5—little different from that of a dye solution to which no viscose sheet had been added—whilst for a relative mass of 0·52 g./100 ml, the *p*Hs were between 4·5 and 5. The hydrogen ions originate from the carboxyl groups in the viscose sheet, and they are transferred to the solution by ion exchange In the commercial sheet, the carboxyl groups are associated with metallic cations, some of them divalent, and these cations are exchanged for hydrogen ions when the sheet is purified by steeping it in N/10 hydrochloric acid. Although the sheet is subsequently washed free from acid, the hydrogen ions of the carboxyl groups in the viscose exchange with sodium ions in solution when the purified sheet is immersed in a dye solution containing sodium chloride. The greater the mass of viscose sheet in a given volume of solution, the greater is the number of hydrogen ions exchanged, and the greater is the consequent fall in the *pH* of the solution. This fall in *pH* occurs whether the concentration of sodium chloride in the solution is 0·5 g. or 10 g. per litre, though for the latter concentration the equilibrium absorption is not appreciably affected by the relative mass of viscose sheet.

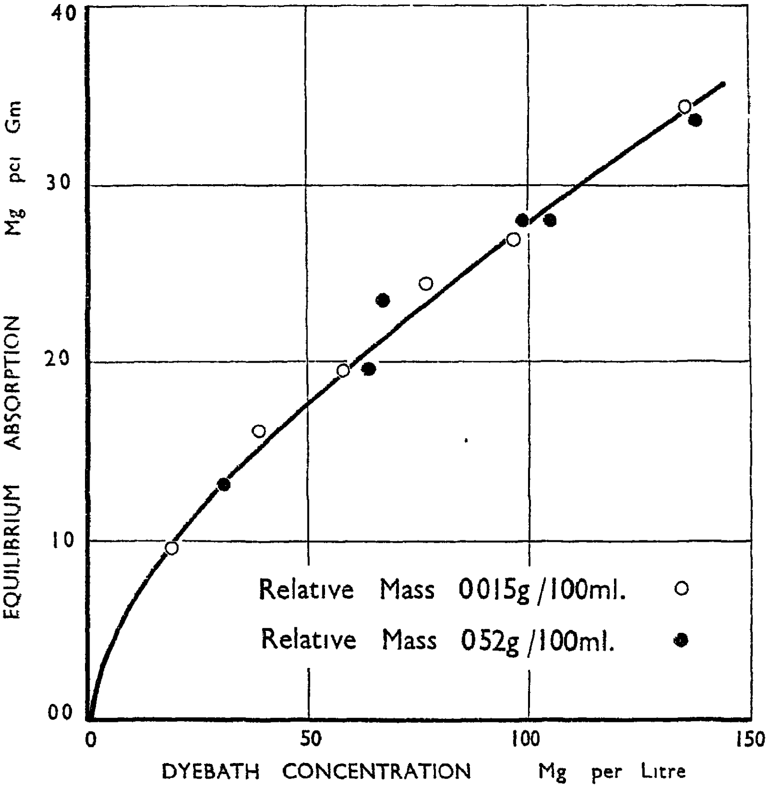

Fig 3

Absorption isotherm of Chrysophenine G on never-dry viscose sheet Dyebaths buffered at *pH* 4 7. Temperature 90°C. Sodium ion concentration equivalent to 0 5 g sodium chloride per litre.

For dye solutions containing 0·5 g. sodium chloride per litre, the variation of the equilibrium absorption with the relative mass of viscose sheet is due entirely to the corresponding change in the *pH* of the dye solution. This was shown by experiments in which the dye solution was buffered at *pH* 4 7 with an acetate buffer in quantity sufficient to give a sodium ion concentration equal to that in a solution containing 0·5 g. sodium chloride per litre. Under these conditions, the absorption isotherms at 90° C. for relative masses of viscose sheet equal to 0 015 g. and 0 52 g. per 100 ml., respectively, were measured, and are shown in Fig. 3. There is seen to be no significant difference between the two isotherms obtained with the buffered dye solutions whereas the isotherms corresponding to the same relative masses of viscose sheet were widely different when the solutions were not buffered (Fig. 1) Moreover the isotherm for the solutions buffered at *pH* 4 7 is in fairly close agreement with that obtained with those unbuffered dye solutions for which the relative mass of viscose sheet was 0 52 g /100 ml. and the *pH*s at equilibrium were between 4·5 and 5. (Fig 1b).

Fig 3 shows the relation between the equilibrium absorption and the concentration of dye in equilibrium solutions containing inorganic electrolyte of constant concentration and buffered at constant *pH*. In contrast to this, Fig. 4 shows the relation between the equilibrium absorption and the *pH* of an unbuffered dye solution in which both the dye concentration and the total cation concentration of inorganic electrolytes are maintained constant. The relative mass of viscose sheet (0 15 g /100 ml) was sufficiently small to ensure that the mass of dye absorbed by the viscose sheet was negligible compared with the total mass of dye in solution Thus the initial and equilibrium concentrations of dye in solution were practically equal, being fixed at 0·097 g. per litre The curve A in Fig. 4 was obtained at 90° C with a total cation concentration of inorganic electrolytes in the equilibrium solutions equal to 0·01M (equivalent to 0 585 g. sodium chloride per litre). These inorganic electrolytes were mixtures of sodium chloride and hydrochloric acid in such varying proportions that the *pH*s of the dye solutions varied from 6 to 2. It is seen that under these conditions the equilibrium absorption increases steadily as the *pH* of the solution decreases and between *pH* 3 and 2 it attains a fairly constant value, which is about 60 per cent higher than the equilibrium absorption at *pH* 6

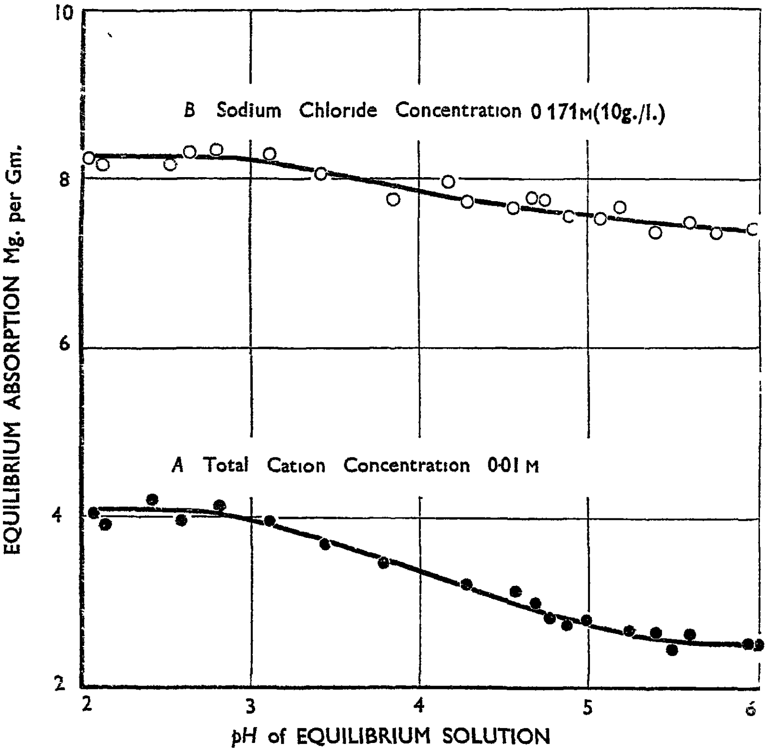

Fig 4.

Variation of the equilibrium absorption of Chrysophenine G on never-dry viscose sheet with the *pH* of the equilibrium solution.

The curve B in Fig. 4 gives the results of similar experiments for which the sodium chloride concentration was 0 171M (10 g /l.) and shows that for this high salt concentration the effect of *pH* on the equilibrium absorption is relatively small. The equilibrium absorption increases slightly as the *pH* of the solution decreases, but below *pH* 3 it attains a fairly constant value which is only about 10 per cent higher than the value at *pH* 6. Thus the results in Fig 4 agree with the observation that the equilibrium absorption of Chrysophenine depends on the relative mass of viscose sheet when the salt concentration is 0 5 g /l , but not when it is 10 g /l

Although the results described here were obtained with never-dry viscose sheet, there is no reason to doubt that similar results would be obtained with Cellophane. An earlier paper described equilibrium absorption measurements of Chrysophenine on Cellophane, and when these measurements were made, the effect of the relative mass of viscose sheet on the *pH* of the dye solutions was not realised In these experiments, the relative mass of viscose sheet was fixed at 0 8 g /100 ml , consequently, although the *pH*s of the equilibrium solutions would not vary appreciably from one experiment to another, they would be low and probably about 4. The present results show that the effect of *pH* on the equilibrium absorption is greatest when the sodium chloride concentration is low. In the earlier measurements with Cellophane, the concentration of sodium chloride was relatively high for many of the isotherms. It is therefore probable that apart from those isotherms for which the sodium chloride concentration was 1 g./l or less, the equilibrium absorptions were not appreciably affected by the high relative mass of viscose sheet used in these experiments.

For the interpretation of the diffusion measurements, absorption isotherms of Chrysophenine G on never-dry viscose sheet were required at 90° C Fig. 5 shows a series of such isotherms for five different sodium chloride concentrations, the relative mass of viscose sheet being 0 015 g /100 ml., and the *pH* of the equilibrium solutions being about 6. As shown by the logarithmic plot in Fig 6, the isotherms approximate to the Freundlich equation

$$[R]_A = k[R]_s^n$$

where $[R]_A$ is the equilibrium absorption of dye on the viscose sheet, $[R]_s$ is the concentration of dye in solution and k is a constant The values of n for the different sodium chloride concentrations are as follows·—

NaCl, g /l. . .	0·5	1	2	5	10
n	0·67	0·67	0·72	0·69	0·72

In the following discussion, the effect of *pH* on the equilibrium absorption is attributed to the presence of ionisable carboxyl groups in the viscose sheet Many direct dyes contain groups that are either weakly basic or weakly acidic, and in consequence the chemical structure and hence the affinity for cellulose of such dyes may depend on the *pH* of the dye solution The Chrysophenine molecule contains no groups of a recognised acidic or basic character, and a potentiometric titration of a Chrysophenine solution with hydrochloric acid showed that the dye did not behave as a weak base

The absorption spectrum of an aqueous Chrysophenine solution, centinormal in hydrochloric acid, is little different from that of a Chrysophenine solution of the same concentration and centinormal in sodium chloride. The maximum extinction coefficient of the solution containing acid is about 2 per cent higher than that of the solution containing sodium chloride These spectra together with the potentiometric titration measurements suggest that the chemical structure of Chrysophenine in aqueous solution is not appreciably affected by the presence of centi-normal acid

DISCUSSION.

The Variation of the Equilibrium Absorption with *pH*.

Neale and his collaborators[2] have investigated the equilibrium absorption of the direct dye Chlorazol Sky Blue FF by acidic oxycelluloses prepared from cotton cellulose by oxidation with hypobromite in alkaline

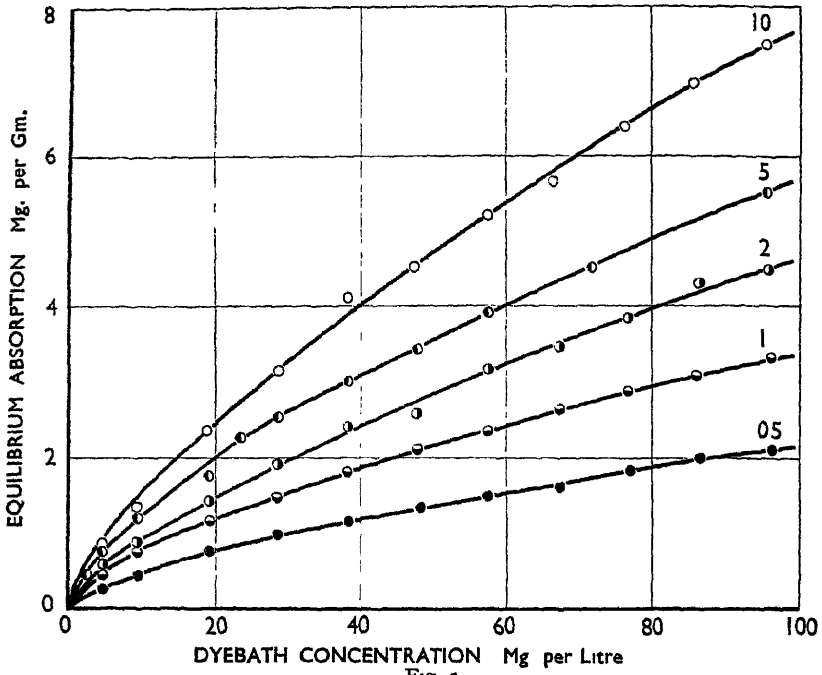

Fig 5
Absorption isotherms of Crysophenine G on never-dry viscose sheet at 90°C
Sodium chloride concentration (g /l) is shown on each isotherm

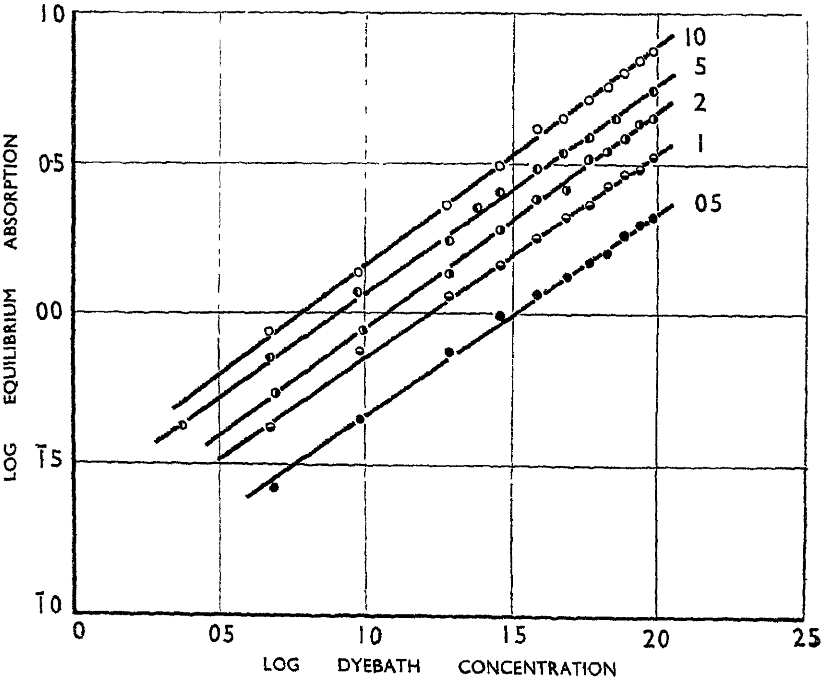

Fig 6
Logarithmic plot of the absorption isotherms of Chrysophenine G on never-dry viscose sheet at 90°C

solution. They showed that the equilibrium absorption of dye from a buffered solution of constant dye and salt concentration decreased with increasing carboxyl content of the oxycellulose. They[3] also showed that for a given oxycellulose, the equilibrium absorption increased as the *pH* of the dye solution was decreased. The latter results are similar to those described here for the absorption of Chrysophenine by viscose sheet, which is to be regarded as an acidic oxycellulose.

Hanson, Neale and Stringfellow[3] concluded that the effect of *pH* on the equilibrium absorption was due to the dependence of the degree of ionisation of the carboxyl groups upon the *pH* of the solution. They showed that their results could be interpreted qualitatively as follows. The dye anions are adsorbed on the cellulose chains, and, in order to preserve electrical neutrality in the cellulose, must hold an equivalent number of sodium ions or other cations in their vicinity. Thus the concentration of sodium ions is greater in the cellulose than in the external solution. The dyed cellulose in equilibrium with the dye solution containing sodium chloride may therefore be considered to consist of two phases—the cellulose phase and the solution phase—in each of which the constituent ions of the dye and the sodium chloride are in aqueous solution. (The cellulose phase also contains dye anions not in aqueous solution but adsorbed on the cellulose.) Since the sodium ion concentrations in the cellulose phase and the solution phase are not equal, the concentrations of any other ion in the two phases also differ, and are related by the Donnan equations of membrane equilibrium. From these equations, it follows that the concentration $[R]_c$ of free dye anions in the cellulose phase is less than the concentration $[R]_s$ of dye anions in the solution phase, $[R]_c$ and $[R]_s$ are related by the Donnan equation

$$[R]_c = \left(\frac{[\mathrm{Na}]_s}{[\mathrm{Na}]_c}\right)^r \cdot [R_s]$$

where $[\mathrm{Na}]_s$ and $[\mathrm{Na}]_c$ represent the sodium ion concentrations in the solution and the cellulose phase respectively, and r is the valency of the dye anion.

The concentration of dye adsorbed on the cellulose chains (i.e. the equilibrium absorption) is assumed to be directly proportional to the concentration $[R]_c$ of free dye anions in the cellulose phase. Thus when the concentration $[R]_s$ of dye anions in the external solution is maintained constant, the equilibrium absorption is directly proportional to the ratio $([\mathrm{Na}]_s/[\mathrm{Na}]_c)^r$ which is less than unity. If ionised carboxyl groups are present in the cellulose, they also will hold sodium ions in their vicinity, and the sodium ion concentration $[\mathrm{Na}]_c$ in the cellulose phase will therefore be increased. Hence the ratio $[\mathrm{Na}]_s/[\mathrm{Na}]_c$, and consequently the equilibrium absorption, will be decreased by the presence of carboxyl ions in the cellulose. Thus if an acidic oxycellulose and a cellulose that does not contain carboxyl groups are dyed to equilibrium in the same dyebath, the equilibrium absorption of dye is smaller on the oxycellulose.

For a given oxycellulose, the proportion of carboxyl groups that are ionised, and hence their effect in diminishing the absorption of dye, depends on the *pH* of the equilibrium solution. If both the dye concentration and the total cation concentration of inorganic electrolytes are maintained constant, then the equilibrium absorption should vary between two limiting values as the *pH* of the solution is varied. At a sufficiently high *pH* all the carboxyl groups will be ionised and the equilibrium absorption will be at a minimum. At a sufficiently low *pH* the ionisation of the carboxyl groups will be completely suppressed, and the equilibrium absorption will be at a maximum. At intermediate *pH*s the carboxyl groups will be partially ionised and the equilibrium absorption, decreasing with increasing *pH*, will be between the two limiting values.

The results shown in Fig. 4 are in accordance with this theory. As the *pH* of the equilibrium solution decreases, the equilibrium absorption increases, and between *pH*s 3 and 2 attains a fairly constant value Although the degree of ionisation of the carboxyl groups will depend directly on the *pH* of the cellulose phase (which will be lower than the *pH* of the equilibrium solution) it is probable that all the carboxyl groups will be undissociated when the solution *pH* is about 2

The Relationship between Substantivity Ratio and Salt/Dye Ratio.

In an earlier paper[1] a general theory of the direct dyeing of cellulose was developed. Its most important consequence was the deduction that the ratio of the equivalent concentration of salt to dye in solution (called the salt/dye ratio) uniquely determines the distribution of dye between the cellulose and the solution (called the substantivity ratio) In the development of the theory no account was taken of the effect of carboxyl groups present in the cellulose on the equilibrium absorption The general equation (11) in the earlier paper,[1] which shows that the salt/dye ratio and the substantivity ratio are uniquely related, was there obtained from free-energy considerations It can be deduced more simply, however, by directly applying the Donnan theory of membrane equilibrium, and it is deduced here in this way, as a particular case of the theory for cellulose containing carboxyl groups in equilibrium with a solution containing sodium chloride and Chrysophenine It is assumed that the *pH* of the solution is about 7 and that the hydrogen ion concentrations in the solution and the cellulose phases are negligible compared with the concentrations of other cations

The Chrysophenine ion is divalent and the dye will be represented by Na_2R. The molar concentrations of the sodium ion, the chloride ion, and the free dye anion, in the cellulose phase will be represented by $[Na]_c$, $[Cl]_c$ and $[R]_c$, respectively, and in the solution phase by $[Na]_s$, $[Cl]_s$ and $[R]_s$, respectively. The concentration of dye anions adsorbed on the cellulose, expressed as moles of dye per 100 g. of cellulose, will be represented by $[R]_A$, and the concentration of carboxyl ions in the cellulose expressed in the same units will be represented by [COO].

The ionic concentrations in the two phases are related by the Donnan equations

$$\left(\frac{[Na]_s}{[Na]_c}\right)^2 = \left(\frac{[Cl]_c}{[Cl]_s}\right)^2 = \left(\frac{[R]_c}{[R]_s}\right) \equiv w^2 \quad . \qquad \ldots \quad (1)$$

where w, which is less than unity, represents the ratio of the concentration of sodium ions in the solution phase to that in the cellulose phase.

Equations (1) may be rewritten as

$$\left.\begin{array}{l}[Na]_c = w^{-1}\ [Na]_s \\ [Cl]_c = w\ [Cl]_s \\ [R]_c = w^2 . [R]_s\end{array}\right\} \qquad (2)$$

Following Hanson, Neale and Stringfellow[3] it will be assumed that the concentration $[R]_A$ of dye adsorbed on the cellulose is directly proportional to the concentration $[R]_c$ of free dye anions in the cellulose phase, i e

$$[R]_A = K[R]_c \qquad . \quad (3)$$

where K is a constant This assumption[4] is a direct application of the Langmuir equation to a system for which the ratio of occupied to total sites is negligible If the value of $[R]_c$, given by equation (2), is substituted in equation (3), then

$$[R]_A = Kw^2\ [R]_s \qquad ..(4)$$

The substantivity ratio is defined as the ratio of the equilibrium absorption $[R]_A$ to the concentration $[R]_s$ of dye in solution. Equation (4) shows that the substantivity ratio is a function of w alone

The condition for electrical neutrality in the cellulose phase is given by the equation

$$[Na]_c = [Cl]_c + 2[R]_c + \frac{1}{W}(2[R]_A + [COO]) \qquad (5)$$

where W represents the volume of water in the cellulose phase and is expressed as litres per 100 g of cellulose

The last term of equation (5) shows the effect of the adsorbed dye anions and of the carboxyl ions in increasing the sodium ion concentration in the cellulose phase above that in solution. The total carboxyl content of the never-dry viscose sheet was 3·0 millimoles per 100 g. of cellulose, hence if all the carboxyl groups are ionised, the total carboxyl ion content [COO] is also 3·0 millimoles per 100 g. It is then comparable in magnitude with the equivalent concentration $2[R]_A$ of adsorbed dye (which for the measurements described here varies from about 0·2 to 2·3 milliequivalents per 100 g.) and might therefore be expected to exert a relatively large effect on the dyeing of the viscose sheet.

Equation (5) gives the ionic concentrations in the cellulose phase and these may be related to the corresponding concentrations in solution by means of equation (2). Thus equation (5) reduces to

$$[Na]_s = w^2[Cl]_s + 2w^3\left(1+\frac{K}{W}\right)[R]_s + \frac{[COO]}{W}\,w \qquad . \quad (6)$$

The salt/dye ratio p is defined as the ratio of the equivalent concentration of salt to dye in solution.

Thus $$p \equiv \frac{[Cl]_s}{2[R]_s} \qquad . \quad (7)$$

and since electrical neutrality is preserved in solution

$$[Na]_s = [Cl]_s + 2[R]_s \qquad (8)$$

whence $$\frac{[Na]_s}{[Cl]_s} = \frac{1+p}{p} \qquad . \quad . \quad . \quad (9)$$

From a combination of equations (6), (7) and (9), the final equation is obtained:

$$\left(1+\frac{K}{W}\right)w^3 + pw^2 + p.\ w\frac{[COO]}{W[Cl]_s} = 1+p \qquad . \quad . \quad (10)$$

When the cellulose does not contain carboxyl groups—a condition to which carefully purified cotton cellulose approaches—then equation (10) reduces to

$$\left(1+\frac{K}{W}\right)w^3 + pw^2 = 1 + p$$

This shows that w is uniquely determined by the salt/dye ratio p providing W, the volume of water in the cellulose phase, is independent of the concentration of salt in the solution. Since the substantivity ratio is a function of w alone, it follows that for a cellulose that does not contain carboxyl groups the substantivity ratio is uniquely determined by the salt/dye ratio. This was the basis of the general deductions of the earlier paper.*

Equation (10) shows, however, that when carboxyl ions are present in the cellulose, the quantity w, and hence the substantivity ratio, depend on the concentration $[Cl]_s$ of salt when the salt/dye ratio p is maintained con-

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* A similar treatment to that above for the general case of a dye represented by A_rR_a and a salt represented by B_sS_b leads, in the absence of carboxyl groups, to the general equation

$$(1 + K/W)\,w^r + pw^s = w^{-a} + pw^{-b}$$

This is identical with the general equation (11) of the earlier paper[1] except that the term $(1 + K/W)$ replaces a different constant X. Another theoretical treatment has recently been given by Crank[4]. All the treatments predict a unique isothermal relation between the substantivity ratio and the salt/dye ratio, providing that the volume of the water in the cellulose phase is independent of the concentration of salt in the equilibrium solution. They differ, however, in the way they deduce from the general equation, an equation to the absorption isotherm obtained when either the salt or dye concentration of the equilibrium solution is maintained constant. The approximation made for the solution of the general equation in the earlier paper[1] was poor and arose from an incorrect interpretation of the constant X. The approximation made by Crank gives an equation to the isotherm in fair agreement with the experimental data stant. The effect of the carboxyl ions on the substantivity ratio is given by the term $pw[COO]/W[Cl]_s$. When the salt/dye ratio p is maintained constant, then the effect of this term is that the value of w—and hence the substantivity ratio—is lower, the higher the value of the carboxyl ion content [COO]. On the other hand, when the salt/dye ratio p and the carboxyl ion content [COO] are maintained constant, the effect of the carboxyl ions on the substantivity ratio decreases as the salt concentration $[Cl]_s$ increases.

The data of Fig. 5 are shown in Fig 7 as a logarithmic plot of the substantivity ratio against the salt/dye ratio. For salt concentrations from 2 to 10 g./l., a unique relation is obtained between these two quantities, but the points for a salt concentration of 0·5 g./l. fall definitely lower than the remainder whilst those for 1 g /l. salt are slightly low. Thus the theoretical depression of the substantivity ratio due to carboxyl ions is shown only by the experimental results for the lowest salt concentrations. As the theoretical depression of the substantivity ratio decreases with increasing salt concentration, it was at first thought that the magnitude of the effect might be too small at the higher salt concentrations to be detected experimentally.

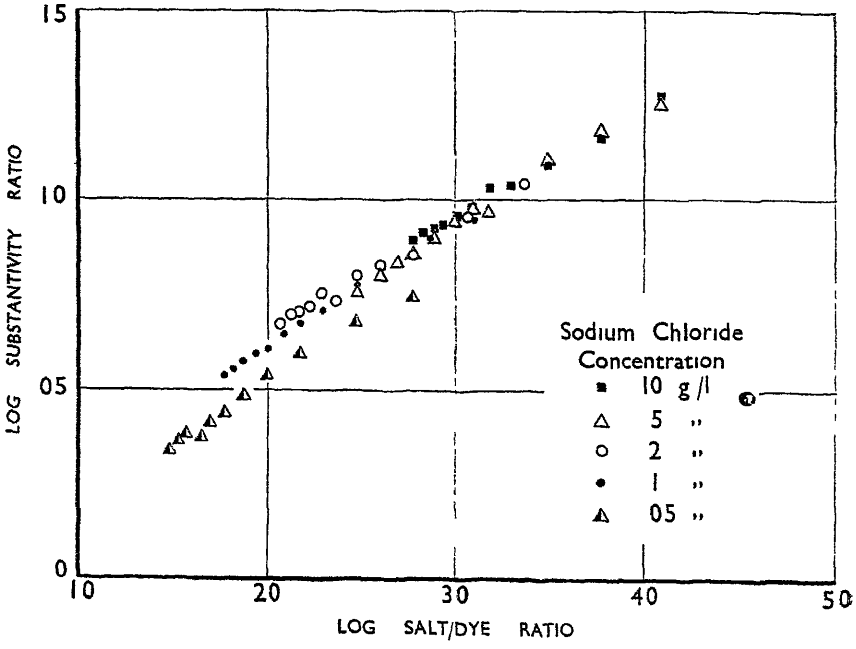


Fig 7

Logarithmic plot of substantivity ratio against salt/dye ratio for the absorption of Chrysophenine G on never-dry viscose sheet at 90°C

From a combination of equations (2), (5) and (8) the following equation is obtained

$$w^{-1}([Cl]_s+2[R]_s)=w[Cl]_s+2w^2[R]_s+\frac{1}{W}(2[R]_A+[COO])$$

In the experimental work, the concentration of dye in the equilibrium solution was generally small compared with that of salt Hence, as an approximation, $2[R]_s$ can be neglected in comparison with $[Cl]_s$, and when this is done the foregoing equation reduces to

$$w^2+\frac{1}{W}\left(\frac{2[R]_A+[COO]}{[Cl]_s}\right)w-1=0 \qquad (11)$$

For a given salt concentration $[\mathrm{Cl}]_s$ this quadratic equation can be solved for w if the values of W and [COO] are known, $[\mathrm{R}]_A$ being experimentally determined. But equation (4) shows that the substantivity ratio $[\mathrm{R}]_A / [\mathrm{R}]_s$ is directly proportional to w^2, and hence the theoretical effect of the carboxyl ions on the substantivity ratio can be calculated when W and [COO] are known.

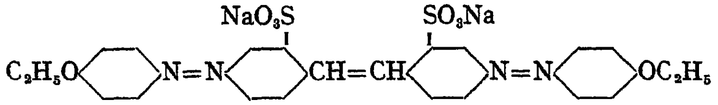
It seems likely that the quantity W should relate to the volume of water in the ionic atmospheres of the adsorbed dye anions, and it may vary with the concentration of salt in the solution. The assumption made by other workers that its value is constant for a given sample of cellulose will, however, be adopted here. Recent attempts by Marshall and Peters[5] to evaluate its magnitude gave the value of 0·045 litre per 100 g. for viscose rayon. This value has been made the basis of tentative calculations from the present experimental data, although its application to never-dry viscose sheet may not be justified.

The value of the carboxyl ion content [COO] is also unknown, and will depend on two factors, (1) the degree of ionisation of the carboxyl groups and (2) the proportion of ionised carboxyl groups that directly affect the absorption of dye. Calculations based on the arbitrary and constant value of 0·045 litre for W show that if the carboxyl ion content [COO] is equal to the total carboxyl content of the viscose (3·0 millimoles per 100 g.), then the substantivity ratio should be considerably reduced even at the highest salt concentrations of 5 and 10 g./l. It should be stressed, however, that these calculations must be treated with reserve on account of the assumptions involved. If they are valid, however, they would suggest that the carboxyl ion content effective in reducing the substantivity ratio, is considerably less than the total carboxyl content of the viscose sheet. This may simply be due to an incomplete ionisation of the carboxyl groups even though the *pH*s of the equilibrium solutions were about 6, i.e. to the fact that the hydrogen ion concentration is considerably higher in the cellulose phase than in the external solution. On the other hand, as Neale and Stringfellow[3] point out, "the distribution of the carboxyl groups in relation to the dye absorbing centres is not known." If some of the carboxyl ions exist in the crystalline regions of the viscose sheet, they might exert little effect on the dye absorption, which is probably confined to the amorphous regions. It is hoped to obtain further information on these points by an investigation now in progress on the absorption of Chrysophenine by acidic oxycelluloses prepared from cotton.

EXPERIMENTAL DETAILS.

Chrysophenine G.

The dyestuff Chrysophenine G (Colour Index No. 365) is a stilbene derivative with the constitution.



It was supplied by Messrs Imperial Chemical Industries (Dyestuffs) Ltd., in batch form, and was purified first by the method of Robinson and Mills[6] and then recrystallised several times from water/alcohol mixtures. Standard solutions were prepared from samples dried at 90° C. in a vacuum oven connected to phosphorus pentoxide tubes. The conductances of these solutions were within 0·5 per cent. of the values obtained for earlier samples; this showed that the purified sample was reasonably free from inorganic electrolytes. The absorption spectrum of an almost completely exhausted dyebath agreed with that of a freshly prepared dye solution of the same concentration; the conclusion was therefore drawn that the purified sample did not contain coloured impurities.

Viscose Sheet.

The viscose sheet was supplied by the British Cellophane Co., of Bridgewater, and was a special batch that had never been allowed to dry since manufacture. This never-dry sheet was kept in distilled water until required for use. It is more highly swollen than the normal Cellophane sheet, the water imbibitions of the two types of sheet being 3·16 and 1·2 g. of water per g. of sheet, respectively. The sheet was freed from soluble impurities, and from metallic cations associated with the carboxyl groups, by first washing in distilled water and then steeping it in 0·1 N hydrochloric acid. Finally, the sheet was washed with successive changes of distilled water until the wash water was neutral, and it was then stored in distilled water. Its ash content was 0·07 per cent. The carboxyl content of the sheet was determined by the measurement of its Methylene Blue absorption according to the method described by Davidson[7] for oxidized cotton, the value obtained being 3·0 millimoles per 100 g.

Equilibrium Absorption Measurement

The never-dry sheet was dyed at 90° C. in resistance glass flasks containing a solution of known dye and sodium chloride concentration. Although preliminary measurements showed that equilibrium was generally attained within 10 minutes, the sheet was dyed for at least 30 minutes during which time the flasks were agitated. The dyed sheet was then removed from the dyebath, rinsed in ice-cold water, blotted and then immersed in a known volume of 20 per cent. pyridine. When all the dye had been extracted, the sheet was dried at 110° C. and its dry weight determined.

The concentration of the dye extracted in the aqueous 20 per cent. pyridine solution was determined by measuring the optical density of the extract at a wave-length of 400 $m\mu$ by means of a photo-electric spectrophotometer. (Chrysophenine is phototropic[1] and the solutions were therefore illuminated before measurement.) Since there are small deviations from Beer's law for solutions of Chrysophenine in 20 per cent. pyridine, the concentrations of the extracts were therefore interpolated from a curve relating optical density and concentration. From the concentration of the extract and the mass of dry sheet, the equilibrium absorptions were calculated as mg. per g. of viscose sheet.

Only the dyebaths used to obtain the results shown in Fig. 3 were buffered. The stock buffer solution was prepared as follows: A mixture consisting of 25 ml. of N/10 acetic acid, 12·5 ml. of N/10 sodium hydroxide and 0·1337 g. sodium chloride was diluted with distilled water to a final volume of 200 ml. For the preparation of each dyebath, a measured volume of the stock buffer solution was mixed with an equal volume of Chrysophenine G of the appropriate concentration.

The equilibrium measurements shown in Fig. 4 were made at 90° C. The dyebaths were prepared at room temperature and although the Chrysophenine precipitated from those dyebaths of relatively low *pH*, it dissolved again when the solutions were heated at 90° C., before the introduction of the viscose sheet.

The results have been shown graphically in Figs. 1 to 5, and the corresponding values, most of which are mean values of two or more measurements, are given in Tables I to V.

Potentiometric Titration and Absorption Spectra.

A 0·5 g./l. Chrysophenine G solution was titrated potentiometrically with N/50 hydrochloric acid by means of a glass electrode. The titration curve so obtained did not differ significantly from that obtained by the progressive addition of N/50 acid to distilled water.

The absorption spectra were measured by means of a photo-electric spectrophotometer, the solutions being illuminated for 15 minutes immediately before each measurement.

Results.

Tables I to III

Effect of Relative Mass of Viscose Sheet on the Equilibrium Absorption of Chrysophenine G

(C) = Dyebath concentration, mg per litre (E) = Equilibrium absorption mg per g

Relative mass of viscose, (*a*) = 0·015 g per 100 ml, (*b*) = 0·52 g per 100 ml

Table I (Fig 1) *Unbuffered Dyebaths containing* 0·5 *g Sodium chloride per litre. Temperature* 90° *C*

a	C	19·3	58	96·8		
	E	0·75	1·50	2·11		
b	C	31·2	32·2	70·2	99·1	103
	E	1·36	1·35	2·27	2·56	2·82

Table II (Fig 2) *Unbuffered Dyebaths containing* 10 *g Sodium chloride per litre. Temperature* 90° *C*

a	C	9·47	19·0	28·6	38·1	47·7	57·3
	E	1·37	2·34	3·13	4·11	4·51	5·20
b	C	10·2	10·9	17·5	24·1	38·2	52·5
	E	1·57	1·63	2·23	2·85	3·81	4·73

Table III (Fig 3) *Dyebaths buffered at pH* 4·7 *Sodium ion Concentration equal to that in a Solution containing* 0·5 *g Sodium chloride per l*

a	C	19	39	58	77	97	136
	E	0·96	1·61	1·95	2·44	2·70	3·45
b	C	31	64	67	99	105	138
	E	1·32	1·96	2·34	2·80	2·80	3·36

Table IV (Fig 4)

Effect of *pH* on the Equilibrium Absorption of Chrysophenine G on Viscose Sheet

Concentration of Chrysophenine in solution, 0·097 g per litre Temperature 90° C, (E) = Equilibrium absorption mg per g

A. Total Cation Concentration of Inorganic Electrolyte 0·01 M

pH	2·07	2·13	2·42	2·59	2·82	3·11	3·43
E	4·06	3·91	4·20	3·94	4·11	3·94	3·69
pH	3·79	4·27	4·57	4·68	4·76	4·87	4·98
E	3·45	3·20	3·14	3·00	2·82	2·73	2·80
pH	5·24	5·39	5·48	5·58	5·86	6·0	
E	2·66	2·65	2·44	2·64	2·52	2·53	

B Sodium Chloride Concentration, 0·171 M (10g /l)

pH	2·04	2·12	2·52	2·64	2·80	3·11	3·42
E	8·24	8·08	8·18	8·31	8·33	8·30	8·05
pH	3·84	4·18	4·27	4·55	4·66	4·73	4·87
E	7·75	7·99	7·71	7·68	7·79	7·75	7·53
pH.	5·08	5·19	5·40	5·60	5·75	5·95	
E	7·53	7·67	7·37	7·47	7·34	7·40	

Table V (Fig. 5)

Absorption Isotherms of Chrysophenine G. on Never-dry Viscose Sheet at 90° C.

Unbuffered dyebaths Relative mass of viscose sheet 0 015 g /100 ml
(C) = Dyebath concentration, mg per litre (E) = Equilibrium absorption, mg per g.

Concentration of sodium chloride, g. per litre.							
0 5	C	4 8	9·6	19·2	28 8	38·5	48·2
	E	0·263	0·452	0·750	0·988	1·17	1 33
0 5	C	57·8	67·5	77 1	86·8	96·4	
	E	1·50	1·61	1·86	2·00	2·10	
1·0	C	4·77	9·56	19·2	28·8	38·4	48 0
	E	0·426	0·753	1·15	1·45	1·80	2·11
1 0	C	57·7	67·3	76·9	86·6	96·2	
	E	2·31	2·65	2·89	3·08	3·32	
2·0	C	4·93	9·88	19·1	28·7	38·4	47·9
	E	0·543	0·881	1·37	1·92	2·40	2·59
2·0	C	57·6	67·2	76·9	86·5	96·0	
	E	3·24	3·48	3·85	4·32	4·49	
5·0	C	2·36	4·73	9 50	19·1	23·9	28·6
	E	0·424	0·718	1·21	1·77	2·27	2·56
5 0	C	38·3	47·8	57 5	71·9	95·9	
	E	3·03	3 42	3·92	4·51	5·51	
10	C	4·67	9 47	19·0	28·6	38·1	47·7
	E	0·874	1·37	2·34	3·13	4·11	4·51
10	C	57·3	66·7	76·4	85·9	95·8	
	E	5·20	5·67	6·40	6·99	7·49	

Table VI

Absorption Spectra of Chrysophenine Solutions containing Sodium Chloride and Hydrochloric Acid, respectively

Concentration of Chrysophenine, 10 mg. per litre Thickness of optical cell, 1 cm
Solution 1. 0·01 N in hydrochloric acid Solution 2. 0·01 N in sodium chloride

Wave length mμ.	Solution 1.	Solution 2	Wave-length mμ	Solution 1.	Solution 2.
	Optical density			Optical density	
380	0·628	0·624	430	0·510	0·508
390	0·687	0·670	440	0·469	0·459
395	0 696	0·681	450	0·418	0 409
400	0·693	0·675	460	0·360	0·352
405	0·656	0·647	470	0·288	0·287
410	0·636	0·623	480	0·214	0·213
415	0·607	0 591	490	0·143	0·141
420	0·575	0·554	500	0·089	0·089

REFERENCES.

[1] Willis, Warwicker, Standing, and Urquhart. *Shirley Inst. Mem*, 1945, 19, 223 or *Trans. Faraday Soc*, 1945, 41, 506.
[2] Neale and Stringfellow *J Soc. Dyers and Col*, 1940, 56, 17
[3] Hanson, Neale and Stringfellow. *Trans. Faraday Soc*, 1935, 31, 1718.
[4] Crank. *J. Soc. Dyers and Col*, 1947, 63, 293.
[5] Marshall and Peters. *J Soc. Dyers and Col*, 1947, 63, 446
[6] Robinson and Mills *Proc Roy Soc*, A, 1931, 131, 576.
[7] Davidson. *Shirley Inst. Mem*, 1947, 21, 47, or *J. Textile Inst*, 1948, 39, T65

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10—AN ENUMERATION PROBLEM IN TEXTILE DESIGN

Part I.

By S. A Shorter

CONTENTS

I Introduction and Summary
II Terminology and General Mathematical Technique
III The Structure of Sub-periodic Designs
IV Enumeration Formulae and Calculations

I. INTRODUCTION AND SUMMARY

In the modern developments of the theory of the technique of formal textile design, a conception of fundamental importance has been that of a recurrent series or "cycle" of "steps," regulating the distribution of elements within an area defined as a single "repeat" by the technique of the process of production of the fabric, for example, in a woven fabric, by the schemes of drawing in the warp and of shedding if for the insertion of the weft. The general principles underlying such distributions are independent of the precise nature of the elements distributed, being applicable, for example, when these elements are merely design "points" defining the mode of intersection of warp and weft of a woven fabric, or at the other extreme, when they are features of an elaborate design In the former instance, the cycle of steps defines a simple type of design, of which the most familiar examples are the ordinary sateens In the latter instance the cycle of steps defines a basis for the construction of more elaborate designs, and in this sphere the importance of its study arises from the almost universal tendency for designs to be based on a mode of sub-division of the design space differing from, and possibly finer than, the technical repeat.

The design, which realizes most simply the cycle of steps, is that in which, on each pick, only a single warp thread is raised within the weftway repeat, and in which each warp thread is raised only once within a warpway repeat Such a design must repeat on the same number of ends as picks, and may be represented by an arrangement of design "points" in a square lattice of the usual type, in which there is one, and only one, point in each row and each column of component lattice squares

The present work, of which this paper is the first part, solves the problem of the enumeration of such designs, and in doing so, formulates a technique indispensible for the adequate development of the theory of the cycle of steps.

This type of design has been the subject of a treatise of some 500 pages by Giovanni Strobino, entitled, "Teoria delle armature fondamentali per tessuti," in which the enumeration problem is propounded, but regarded as presenting insuperable difficulties

In what follows the term "elementary design" will be used as the equivalent of Strobino's "armatura fondamentale," since there is some difference of opinion, among writers on the general subject of design, as to what designs should be regarded as "fundamental," this difference arising naturally from the different methods of approach to the subject that are possible. In contexts where there is no possibility of ambiguity the simple term "design" will be used.

There is a considerable body of literature relating to the most familiar type of elementary design, the ordinary sateens, both in their direct aspect, and where they are regarded as specifying modes of distribution of decorative elements and of subdivision of the design space There is, however, scarcely any literature relating to the general class of elementary design Even Strobino's treatise deals mainly with ordinary sateens, and touches only lightly on the more general topic in some 65 pages of text. Moreover, according to P. Rodon y Amigo the wider aspects of the subject have not hitherto been the subject of systematic study ("El trazado de figuras geometricos sobre escalonamiento irregulares no lo hemos visto studiendo por ninguin autor").[1] It is true, however, that some consideration has been given to the distribution of figures on the basis of the so-called "irregular sateens".[7,8]

Section II of this paper deals with certain mathematical preliminaries which are indispensible, not merely to the solution of the enumeration problem, but to future developments of the theory of the elementary design Three methods of specifying a design are considered, respectively, by means of (1) a square lattice containing a single repeat of the design, (2) a set of numbers specifying the positions of the design points in such a lattice, and (3) a "cycle of steps." The third method makes use, in a precisely defined manner, of the well-known concept of a "step" and has the merit of yielding a unique mode of specification Each cycle of steps corresponds to a number of "arrays of steps" which may be cyclically permuted without changing the cycle represented. The necessary and sufficient conditions for a set of terms to represent an array of steps are deduced, so that in essence the problem of enumeration is reduced to that of the enumeration of a particular type of cyclical permutation. As with other problems of this kind the relation between "arrays" and "cycles" is complicated by the existence of cycles which consist of two or more repetitions of a sub-cycle In the present instance such cycles represent a special type of design, which is here termed "sub-periodic." Considered merely geometrically (*i.e.* apart from the weaving process) these designs repeat over an area which is a submultiple of that of the technical repeat. The special conditions, necessary and sufficient for a set of terms to represent an array of steps of a subperiodic design, are deduced, and from a consideration of these conditions in Section III, the general structure of these designs is elucidated, and it is shown how the general enumeration problem involves that of the enumeration of the various types of sub-periodic design. In Section IV enumeration formulæ are obtained and their use is exemplified for designs, for which the numbers of ends and picks on which they repeat range from 2 to 16

In the Shorter Oxford Dictionary the word "enumeration" is given two meanings, "1. the action of finding the number of anything, 2. the action of specifying *seriatim*" The former meaning is the more usual in mathematics, and is the one applicable in the present paper. The problem of enumerating elementary designs by means of a systematic detailed specification is, however, one requiring solution, and it will be considered in Parts II and III of this work.

II. TERMINOLOGY AND GENERAL MATHEMATICAL TECHNIQUE

Use will be made of the customary method of placing design "points" inside the small squares of a lattice formed by two mutually perpendicular sets of equidistant parallel lines, these points being regarded, for the purpose of specifying distances, as situated at the centres of the squares they occupy These design points will be referred to simply as "points" where there is no danger of confusion with geometrical points, such as the points of intersection of lattice lines. The small squares will be termed "lattice squares," and the side of a lattice square will be taken as the normal unit of length. The usual method of specifying the position of a point, design or merely geometrical, by its co-ordinates, will be adopted, the origin being taken at the centre of a lattice square, the x and y directions being respectively weftway to the right and warpway upwards The co-ordinates of design points will thus be integers, positive or negative The number of lattice squares on which a design repeats, warpway and weftway, will be termed the "period" of the design, and will be denoted by the symbol m. It is, of course, the distance between adjacent points along a row or column of lattice squares. If (x, y) and (x', y') are two design points corresponding to repeats of the weaving process, the number x and x' will leave the same remainder when divided by m, and the same is true of y and y': or in the notation of the theory of consequences, $x \equiv x'$ (mod m) and $y \equiv y'$ (mod m), the period m being thus the modulus of the congruences. Because of such congruences, many writers refer to the period as the modulus of the design, but in the present paper this seems undesirable, as it will be necessary to consider congruences relative to other moduli Nevertheless, for convenience, sets of points, any pair of which have co-ordinates satisfying congruences such as the above, will be termed congruent, and the same epithet will be applied to lattice squares whose centres are thus congruent. and a displacement between two congruent points will be termed a congruent displacement

An arrangement of design points inside a square of side m, placed so that its sides lie along lattice lines, will be termed a "representative point arrangement," abbreviated in singular and plural to R P.A. A square of side m placed so as to display an R P.A. will be termed a "design square." It is useful to regard it as movable over an extended design: imagining for example, a sheet of opaque material, with a square hole cut in it, to be moved over the design Starting from some initial position, marked permanently by thickened lattice lines, and moving either warpway or weftway, the original R.P.A. cannot be reproduced until a complete period has been traversed. There are, therefore, at least m R.P.A. corresponding to any given design. On the other hand, there cannot be more than m^2 R.P.A., for there are not more than m^2 positions of the movable design square which are not entirely outside the original marked square, and which therefore do not yield an R.P.A. identical with one previously obtained

Positions of a design square which yield the same R.P.A will be termed "isographic". Congruent positions are necessarily isographic, but the converse of this is not true It will be convenient to refer to an isographic displacement meaning, of course, one which applied to a design square does not result in any change in the R P.A displayed Points or lattice squares which define isographic positions will be termed isographic points Designs which possess non-congruent isographic points belong to a relatively rare but important class, the study of which is an indispensible preliminary to the solution of the enumeration problem

The specification of a design. The most obvious way of specifying an elementary design is to draw one of its R P.A. A more concise method is to state the co-ordinates of the design points within a design square, giving the lowest row and extreme left-hand column the co-ordinate value 1 Assuming that the x values are taken in the order, 1, 2 m, a single array of numbers representing the corresponding y values is a sufficient specification. Such an array is a permutation of the numbers 1, 2, ... m, taken m

at a time without repetition The complete set of $m!$ such permutations represents all the designs of period m, but it does so in a highly repetitive manner, each design being represented by a number of permutations ranging from m to m^2

A permutation of this kind will be called an "array of co-ordinates" Such an array may be cyclically permuted without changing the design that it represents, this process corresponding merely to a weft-way shift of the design square. Even if one considers an array to stand for itself and all its cyclical permutations, thus representing a "cycle of co-ordinates", different cycles may be obtained by adding a constant number to each term, replacing terms greater than m by the congruent (mod m) term in the range $1, 2 \dots m$, this process corresponding to a warp-way shift of the design square.

A unique method of specification may be obtained by making use of the concept of the "step", this being defined for the purpose of the present discussion as the warp-way component of the displacement from a design point in one column of lattice squares to the point next above it in the contiguous column to the right From an array of co-ordinates $y_1, y_2 \dots y_m$ an array of steps is formed by a process of subtraction of consecutive terms, yielding the terms y_2-y_1, y_3-y_2, $\dots y_m-y_{m-1}$ and finally y_1-y_m, adding m to any negative term, thus giving the number, congruent (mod m), in the range 1 to $m-1$ Cyclically permuting any given array of co-ordinates merely does the same to the derived array of steps, while adding a constant number to the terms of the original array of co-ordinates has no effect Hence a design is represented by a unique "cycle of steps" This expression will be taken to denote a cycle of m terms derived from a cycle of co-ordinates, though for certain designs this may be divisible into two or more sub-cycles. The set of points generated by the process of "stepping" according to a prescribed cycle will in general, for a single repeat, yield points outside the range of a single design square The points generated in this way will be termed a "ladder of points", and it will sometimes be convenient to regard the design as specified by m successive points of this "ladder", rather than by m points within a single design square

If on a design lattice one inserts a point p_1, and steps from it according to a prescribed array of steps $s_1, s_2 \dots s_m$, inserting points p_2, p_3, *etc.*, the penultimate step will give the point p_m and the final step s_m will give a point p_{m+1} congruent with p_1 Since p_1 and p_{m+1} are congruent points, the sum of the steps of the complete array is given by

$$s_1+s_2+\dots+s_m=Mm \quad \dots \quad (1)$$

where M is an integer. The array of steps, in addition to conforming to this equation, must fulfil the further condition that no sum of less than m consecutive terms must be divisible by m, for otherwise there would be two points in the ladder, such that the points respectively congruent with them within a single design square would be in the same row of the square. These two necessary conditions are also sufficient to ensure that an array of m assumed steps actually represents a design: for conformity with equation (1) ensures the correct periodicity, while the further condition ensures that the derived array of co-ordinates consists of a permutation of the numbers $1, 2, \dots m$, taken m at a time without repetition

If a design has isographic non-congruent points, the sequence of steps must be the same from each such point, so that the complete array must consist of two or more repetitions of a sub-array, for example, of a set of a terms $s_1, s_2 \dots s_a$ repeated n times, where $na=m$. Cyclically permuting the complete array does the same to the sub-array, so that one may speak of a "sub-cycle" of steps.

Designs of this kind will be termed "sub-periodic". In a warp or weft direction a design square must, of course, always be displaced a full period before the original R P.A is reproduced It is only in an oblique direction that an isographic displacement is possible within a design square

The general rules previously enunciated regarding the complete sum of the terms of the array and a partial sum of consecutive terms, assume special forms with sub-periodic designs Equation (1) becomes

$$n(s_1+s_2+\ldots+s_a)=Mm \qquad (2)$$

or

$$s_1+s_2+\ldots+s_a=Ma \qquad (3)$$

Moreover n and M must be mutually prime, for otherwise, dividing equation (2) by their G.C.M. would yield an equation expressing the fact that a partial sum of consecutive terms is divisible by the period It is further necessary that no single term or sum of consecutive terms within the sub-array should be divisible by a For if such a sum or a single term were equal, say, to pa, it would be possible to find an integer q such that $qMa+pa$, which is a partial sum of consecutive terms, is divisible by m, i e such that $qM+p$ is divisible by n This involves solving the equation $nr-Mq=p$ for r and q in integers, which is always possible, since all allowable values of n and M are mutually prime.

As regards the sufficiency of these special rules a qualification is necessary. Among the sub-arrays conforming to them, there will be some which consist of two or more repetitions of a submultiple sub-array, and these will yield a design for which the value of a is a submultiple of the prescribed value. The rules thus ensure that the design represented has either the prescribed value of a or a submultiple of it, and an exhaustive enumeration according to the rules will include all such additional designs

If a design is non-sub-periodic there will be no isographic displacement within the ambit of a single design square, so that the design has m^2 R P A If the sub-cycle $s_1 s_2 \ldots s_a$ of the design $(s_1 s_2 \ldots s_a)^n$ is not divisible into submultiple sub-cycles, an isographic displacement cannot have a weft-way component less than a. Hence the lattice squares in the first a columns of a design square are all mutually non-isographic, so that the design must have at least $am(=m^2/n)$ R P A. It cannot have more than this number since each of these lattice squares is isographic with squares in other columns of the design square, being in fact one of a set of n mutually isographic squares.

Owing to this varying relation between designs and R.P A., the general problem of the enumeration of elementary designs involves the subsidiary problem of the enumeration of the different types of sub-periodic design This entails in the first instance a closer study of sub-periodicity, and this is made in the next Section

When the sub-cycle of steps consists of a single term, the design represented is a simple twill or an ordinary sateen, according as this term is or is not equal to 1 or $m-1$ It is a great convenience to have an expression to denote either of these two special types of design, and for this purpose the term "sateen-twill" will be used in this paper

For a sateen-twill, equation (3) reduces to $s=M$, and the rule that n and M should be mutually prime, to the well-known rule regarding the step and period of a sateen (obeyed also by a twill) The rule relating to the partial sum of consecutive terms becomes irrelevant since no term can be described as "within" the sub-array

III. THE STRUCTURE OF SUB-PERIODIC DESIGNS

Consider an extended repeat of the design $(s_1 s_2 \ \ldots \ s_a)^n$. Let a super-lattice of mesh a be superposed on the design by thickening every ath lattice line, horizontal and vertical, thus dividing the design space into "cells" of side a Consider a set of points selected from a ladder of points by taking every ath point, for example, the set P_1, P_{a+1}, P_{2a+1}, *etc* It will be seen that every one of these points will occupy corresponding positions in their respective cells—if, for example, one occupies the third column and fifth row of its cell, so will all the others That the columns correspond is obvious from the mode of selecting the points; that the rows correspond follows from equation (3). The complete ladder of points contains n such sets, each having a common within-the-cell position, which will be seen to be different for each set as regards both columns and rows. As regards the columns, this is obvious from the mode of selection of the points: as regards the rows this follows from the condition that no partial sum of consecutive terms of the sub-array must be divisible by a.

Suppose now that one erases all the points except those of a single set and the points congruent with them, and in addition erases all the lattice lines except those of the super-lattice; and finally completely blackens each cell containing a point. This gives a design on an enlarged scale in which the unit of length is the cell-side. In terms of this enlarged unit, the period of the design is n, and the step of the new design point formed from the point P_1, to that formed from P_{a+1} is equal to $(s_1+s_2+\ \ldots+s_a)/a$ or M, the new design being formed from a uniform ladder of points and their repeats on a period n. Since M must be prime to n, this process of stepping will generate a sateen-twill. The step M will in general be greater than n, and may be replaced by the remainder left when M is divided by n. Denoting this reduced step by S, one thus has the relations $S \equiv (s_1+s_2+\ldots+s_a)/a (\text{mod. } n), S<n$.

Sub-periodicity exemplifies in a special manner the general process of the "enlargement" of designs. In this, the design points of a given basic design are "enlarged" into a "motif" consisting of a number of points in a finer lattice. In general the enlargement may be based on any type of design, and where as in the present instance, the basis is a sateen-twill, the area of repeat, as defined by the weaving process, is a multiple of the actual minimum area of repeat

With a sub-periodic elementary design, any a points whose x-co-ordinates are mutually all non-congruent (mod a) may be regarded as forming a motif, the sateen-twill distribution of which would generate the complete design In particular instances the visual appearance of the design may, of course, suggest a definite motif, as for example, when a points within a single cell are distributed on a sateen basis. (The design $(2,14,5)^5$ is of this kind)

The number n will be called the "order" of the sub-periodicity, and the number a the "mesh". For a given period, these two numbers are alternative methods of specifying one of the two characteristics of the sub-periodicity, the other being the step S of the sateen-twill basis of enlargement. The symbol n/S will be adopted to specify this basis. For a prescribed value of n, the step S may have any value less than n and prime to it; and the customary symbol $\phi(n)$ will be used to denote the number of such values If one writes $b=Sa$ the number b is the step measured in the original unenlarged units, its complete range of possible values for all values of n being from 1 to $m-1$ inclusive. Since $S=b/a$ and $n=m/a$, and since S and n are mutually prime, it follows that a is the G C.M. of m and b. Hence for a given period, the basis is uniquely determined by the value of b, and since conversely a given basis uniquely determines the value of b, it follows that the number of possible bases is $m-1$. (This result is in accordance with a well-known theorem in the Theory of Numbers)

Those values of b which are prime to m give $a=1$, and correspond to the ordinary sateen-twills, representing the limiting case of enlargement when the ratio of linear enlargement becomes equal to unity (when the period is a prime number, the only possible sub-periodic designs are, of course, the ordinary sateen-twills)

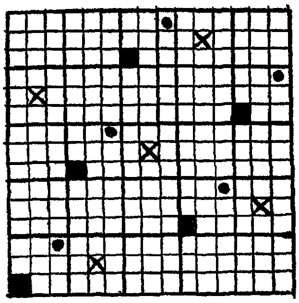

Fig 1

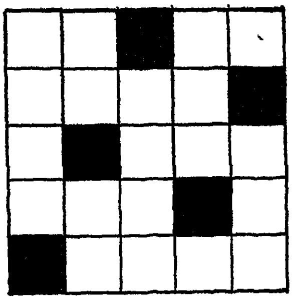

Fig 2

To illustrate the above discussion, one of the R.P.A. of the design $(10, 7, 4)^5$ is shown in Fig. 1. For a design such as this, of order 5 and mesh 3, there are three sets of five points in a single repeat of the ladder constituted as follows.

$$\begin{array}{lllll} P_1 & P_4 & P_7 & P_{10} & P_{13} \\ P_2 & P_5 & P_8 & P_{11} & P_{14} \\ P_3 & P_6 & P_9 & P_{12} & P_{15} \end{array}$$

This division of the points into three sets is indicated by the use of three different kinds of mark. The enlarged sateen-twill derived from the set $P_1 P_2 \ldots P_{13}$ in the manner described above is shown in Fig. 2 The step S is given by the congruence $S \equiv (10+7+4)/3 (\text{mod } 5)$, and the inequality $S<5$, and is thus equal to 2, so that the basis of enlargement is the 5/2 sateen.

IV. ENUMERATION FORMULAE AND CALCULATIONS

In this Section the following notation will be adopted To denote the total number of elementary designs of any given period, the symbol X will be used with a subscript symbol indicating the period. To denote the number of sub-periodic designs of any given period and mesh, the symbol Y will be used with two subscript symbols, the first indicating the period and the second the mesh. and to denote the number of R P A of such designs the symbol R will be used similarly. Thus the total number of designs of period m is X_m, the number of sub-periodic designs of period m and mesh a is Y_{ma}, and the corresponding number of R P.A. is R_{ma} The sign of summation Σ applied to an expression containing Y or R will indicate summation with respect to the symbol indicating the mesh, extending over all values, including unity, which are sub-multiples of a number indicated as a subscript to the sign of summation Thus $\underset{a}{\Sigma_i} Y_{mi}$ represents the result of summation over all the values of i, including unity, which are sub-multiples of a.

Consider the process of forming the R.P.A. of designs of period m and mesh a. As in the previous section, let $n=m/a$. Let a design square be divided into cells of side a by means of thickened lattice lines Consider first the number of R.P.A. which may be formed for a prescribed basis of enlargement This number is equal to the number of allowable ways of placing points in the first a columns of the design square, for these points form a motif which in conjunction with the prescribed basis determines the complete R.P A. The point in the first column may be placed in any one of an positions This points and its sateen-twill distributed points monopolize n rows of the design square, so that there are only $an\text{-}n$ positions available for the point in the second column. Similarly there are only $an\text{-}2n$ positions available for the point in the third column, and so on The number of ways of filling the first a columns is therefore

$$an(an\text{-}n)(an\text{-}2n)\ldots \text{ to } a \text{ terms or } a!\,n^a$$

Since the number of possible bases of enlargement is $\phi(n)$ the total number of R P.A. which may be formed is $a!n^a\phi(n)$. The method of formation of the R P.A. is such as to include all those of designs whose mesh is a sub-multiple of the prescribed mesh; so that in place of equating the above number of R P.A to R_{ma}, it is necessary to write

$$R_{ma}+\sum_{a} R_{mi}=a!\,n^a\phi(n) \qquad \ldots(4)$$

The relation between the numbers of designs and R P A deduced for sub-periodic designs in Section II is expressed, in the present notation, by the equation

$$R_{mx}=mxY_{mx} \qquad \ldots(5)$$

where x is any allowable value of the mesh Making use of this relation to convert the R values of equation (4) to Y values, leads to the equation

$$aY_{ma}=(a-1)!\,n^{a-1}\phi(n)-\sum_{a} iY_{mi} \qquad (6)$$

by means of which, for any prescribed period, the sub-periodic designs of the various possible orders, are readily enumerated

When $a=1$, the designs are merely the ordinary sateen-twills, and this equation yields the known result

$$Y_{m1}=\phi(m) \qquad (7)$$

When $a>1$, and is a prime number, the only sub-multiple mesh is unity, and the equation reduces to

$$aY_{ma}=(a-1)!\,n^{a-1}\phi(n)-\phi(m) \qquad (8)$$

Illustrative calculations for a few periods are given below. In these, and elsewhere, where there is no doubt as to the value of the period, the different Y values are distinguished by a single suffix indicating the mesh.

$m=4$

The allowable values of the mesh are 1 and 2, both prime. Hence

$$Y_1=\phi(4)=2$$

$$Y_2=\frac{1!2^1\phi(2)-\phi(4)}{2}=0$$

$m=6$

The allowable values of the mesh are 1, 2 and 3, all prime. Hence

$$Y_1=\phi(6)=2$$

$$Y_2=\frac{1\ 3\cdot\phi(3)-\phi(6)}{2}=2$$

$$Y_3=\frac{2!2^2\phi(2)-\phi(6)}{3}=2$$

$m=12$

The allowable values of the mesh are 1, 2, 3, 4 and 6. For the prime values, calculations similar to the above, give $Y_1=4$, $Y_2=4$, $Y_3=20$. and for the two other values, the calculations are as follows:

$$Y_4=\frac{3!\,3^3\phi(3)-(2\cdot 4+4)}{4}=78$$

$$Y_6=\frac{5!\,2^5\phi(2)-(3\cdot 20+2\cdot 4+4)}{6}=628$$

A formula for the calculation of the number of non-sub-periodic designs may be obtained by equating the total number $m!$ of R.P.A. to the sum of the numbers of R.P.A. of the separate types of designs, making use of the appropriate form of equation (5) for the sub-periodic designs, and of the fact that the non-sub-periodic designs have m^2 R.P.A. The resulting formula is identical with that obtained by writing $a=m$ and $n=1$ in equation (6) and interpreting the symbol Y_{mm} as the number of non-sub-periodic designs, thus regarding non-sub-periodicity as the limiting case of sub-periodicity when the mesh becomes equal to the period. The formula is

$$mY_{mm}=(m-1)!-\sum_m iY_{mi} \quad \ldots \quad \ldots \quad (9)$$

For the period 12, for example, this takes the form

$$12Y_{12\cdot 12}=11!-(Y_1+2Y_2+3Y_3+4Y_4+6Y_6)$$

which, making use of the Y values previously calculated, gives $Y_{12\cdot 12}=3{,}326{,}054$.

The total number of designs is, of course, the sum of the numbers of the different types, *i.e.*

$$X_m=Y_{mm}+\sum_m Y_{mi} \qquad (10)$$

Thus $X_{12}=3{,}326{,}054+628+78+20+4+4=3{,}326{,}788$

Eliminating Y_{mm} between equations (9) and (10) gives

$$mX_m=(m-1)!+\sum_m (m-i)Y_{mi} \quad \ldots \quad \ldots \quad (11)$$

expressing X_m in terms of the numbers of sub-periodic designs only; and for prime periods this reduces to

$$mX_m=(m-1)!+(m-1)^2 \quad . \quad . \quad (12)$$

Thus for the period 7,

$$X_7=\frac{6!+6^2}{7}=108$$

The results of these enumeration processes for periods up to 16, are given in the Table. For the non-sub-periodic designs, the allowable values of the mesh are given in order of magnitude as a single line of numbers under the appropriate heading, and the related values of the number of designs are given similarly in corresponding order. Thus for the period 12, the Table shows that the allowable values of the mesh are 1, 2, 3, 4 and 6, and that for these values the numbers of designs are respectively 4, 4, 20, 78 and 628.

In his treatise Strobino correctly envisages the possibility of reducing the general problem to that of enumerating the various types of design which do not possess "scoccomenti irregolari totali" (*i.e.* the various types of sub-periodic design); but in the absence of adequate insight into their structure, he is unable to solve this subsidiary problem, and indeed regards it as practically insoluble.[1] He is able, however, to enumerate the designs of prime

Enumeration of the Elementary Design

Period	Sub-periodic Designs		Number of Non-sub-periodic Designs	Total Number of Designs
	Mesh	Number		
2	1	1	0	1
3	1	2	0	2
4	1. 2	2 0	1	3
5	1	4	4	8
6	1. 2. 3	2 2 2	18	24
7	1	6	102	108
8	1. 2. 4	4. 2. 10	624	640
9	1. 3	6. 10	4,476	4,492
10	1. 2. 5	4 8 76	36,248	36,336
11	1	10	329,980	329,900
12	1 2. 3. 4. 6	4 4 20 78. 628	3,326,054	3,326,788
13	1	12	36,846,276	36,846,288
14	1 2 7	6 18 6582	444,783,906	444,790,512
15	1. 3. 5	8. 64 776	5,881,865,808	5,881,866,656
16	1. 2. 4. 8	8 12 184 80544	81,729,607,780	81,729,688,428

period, since all that is required is a knowledge of the number of sateen-twills. He is thus reduced to what he terms an "experimental investigation," which in essence is a process for eliminating repetitiveness from the complete set of $m!$ arrays of co-ordinates. First, this number is reduced to $(m-1)!$ by selecting only those arrays with the term 1 in the first place (the rejected arrays being merely cyclical permutations of these). From these $(m-1)!$ arrays, 2×2 repeats are drawn and by an examination of these, repetitions are eliminated. This process is illustrated in full detail for the periods 3 and 4. Strobino displays also the R.P.A. ("punteggiature") of the designs of periods 5, 6, 7 and 8, but it is not clear whether or not these were obtained by a similar process (which would be excessively laborious for the larger periods, involving, with the period 8, for example, the drawing and examination of 5040 two by two repeats containing in all 161,280 design points). He abbreviates to some degree this cumbrous method of specification by regarding each R.P.A. as representing itself and its reflexion in a mirror placed with its plane normal to the plane of the design, intersecting it along a warpway line; and he uses special symbols to denote whether or not this reflexion yields a different design. These symbols indicate, of course, the absence or presence of a particular type of symmetry. For example, in the case of designs of period 6, he displays 14 R.P.A., of which 10 are marked as standing for two designs and 4 as standing for only one, yielding a total of 24 in agreement with the result given above[5] Strobino, however, gives 14 as the number of designs, but it will be clear that this is an arbitrary figure, obtained by taking account of only one of the possible types of symmetry. He regards, for example, the design 112143 as the same as 325455, its reflexion in a warpway mirror; but as different from 341211, which is the result of turning it upside down.

In taking account of symmetry, all possible types should be considered This leads to the drawing of a clear distinction between two essentially different concepts, first, that of an elementary design, whose individuality depends upon a certain relative arrangement of points, and also on the relation of this to an external frame of reference; and secondly, that of a new entity, whose individuality depends only on the former of these two characteristics. For convenience of reference this latter entity will be termed a "primitive pattern." The relation between these two entities will depend on the relevant types of symmetry which are possible. These types relate to invariance to such reflexions and rotations as maintain, with possible interchange, the two original directions of the lattice lines. (For example, of the axial and central symmetries possessed by the so-called "square" sateens, only the latter is relevant.) In the absence of any of these symmetries, a primitive pattern corresponds to eight designs, but owing to the possible relevant types of symmetry, this number may be reduced to four, two or even only one. For example, among the designs of period 8, the design 11122764 is one of a set of eight corresponding to the same primitive pattern, the design 11122522 is one of a set of four, the design 12467642 is one of two, and the design 16427246 is the only design derivable from its related primitive pattern

The detailed enumeration of the designs of any period may be abbreviated by specifying one only of each set of designs corresponding to the same primitive pattern, with some indication of how the remainder are derived: and this procedure will be adopted in Part III of the present work. The necessary preliminary study of the types of symmetry relevant to the abbreviation of the enumeration process will be carried out in Part II. It is of interest apart from this particular application

REFERENCES

[1] P Rodon y Amigo *Tecnologia de los tejidos a la Jacquard*, II Decoracion textil, p 84.
[2] Giovanni Strobino *Teoria delle armature fondamentali per tessuti*. (Editoriale Laniera S A 1936) p 121
[3] *Ibid*, p 129.
[4] *Ibid*, p 123.
[5] *Ibid*, pp. 83-120
[6] *Ibid*, p 94.
[7] Watson *Textile Design and Colour* Fourth Edition, p 513 (Longmans Green & Co. 1936)
[8] Enrico de Meo *La technica tessile della decorazione delle stoffe* Part IV (Casa Editrica E Cavalleri Corno, 1936)

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11—THE FRACTIONATION OF STARCH

PART I—THE ESTIMATION OF AMYLOSE IN THE PRESENCE OF AMYLOPECTIN

By R S Higginbotham and G. A. Morrison

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The estimation of amylose in the presence of amylopectin is complicated by the fact that the amyloses and amylopectins of different starches are not chemically or physically identical, although amylose and amylopectin are chemically rather similar since both consist of glucose residues joined principally by 1-4 α-glucosidic linkages. Amylopectin molecules are highly branched and are, in general, larger than amylose molecules, which are believed to be substantially unbranched The proportion of non-reducing terminal glucose units is approximately 0·2 per cent. for amylose and 4 per cent. for amylopectin, and amylose contains about five times as many reducing groups as amylopectin. Both polysaccharides yield maltose on treatment with β-amylase, only amylose is quantitatively converted to maltose, the maximum yield from amylopectin being about 55 per cent.

The amyloses and amylopectins are, however, sharply differentiated by their reactions with iodine, and this is the basis of all the practicable methods for estimating amylose. These depend either upon the potentiometric determination of the amount of iodine absorbed under specified conditions,[1] or upon measurement of the colour-intensity of the iodine complex.[2,3,4,5,6,7] The authors have investigated methods of both types. The former appears to be the more accurate and has the advantage that conditions can be chosen under which the pure unfractionated amyloses of the common starches (sago, potato, tapioca and maize) absorb the same amount (21 per cent.) of iodine, whereas amylopectins absorb a negligible amount (0·5 per cent or less). Only simple apparatus is required, and a procedure in which the only special equipment is a sensitive galvanometer is described in the present paper. Colorimetric methods are more convenient, but the iodine complexes of the amyloses and amylopectins of different starches have different absorption characteristics,[7] for which due allowance must be made.

1. POTENTIOMETRIC TITRATION

The difference in the affinities of amylose and amylopectin for iodine, first demonstrated by Bates, French and Rundle[1] by potentiometric titration is illustrated by the results (Fig. 1) for pure potato amylose[8] and pure potato amylopectin[8] titrated with iodine at 25° C. in the presence of 0·05N potassium iodide and 0·05N potassium chloride. For both materials the percentage of iodine bound is a function of the concentration of free iodine, but there is a well-marked discontinuity with amylose, which at iodine concentrations of the order concerned in Fig. 1 binds far more iodine than does amylopectin. With increasing concentration of iodine (Fig. 2), the amount of iodine absorbed by amylopectin gradually approaches that absorbed by amylose It has been suggested[1,7] that the first stage in the absorption of iodine by amylose is the formation of a complex in which the amylose molecules are coiled into helices having about six glucose units per turn and containing iodine molecules and tri-iodide ions At the point B (Fig. 1) all the amylose helices were assumed to be filled to their maximum capacity and thereafter iodine was presumed to be bound by "adsorption". It has been customary so far to characterise samples of amylose by the amount of iodine bound at the point D; BC is assumed to be linear, and is extrapolated to correct for any adsorption occurring in the first stage of the absorption process. It has been shown, however, that for pure amylose BC is not linear but an exponential curve (Fig. 2), and a straight line is obtained when the percentage of iodine bound is plotted against the logarithm of the concentration of free iodine (C) from $C=10^{-6}$ (20 per cent iodine bound) to $C=5\times10^{-3}$N (24·5 per cent. iodine bound) Thus the points B and D have no special significance, and the first stage of complex formation is presumably complete when somewhat less than 20 per cent. of iodine has been absorbed. It has not been possible to determine accurately the point of discontinuity on the logarithmic graph.

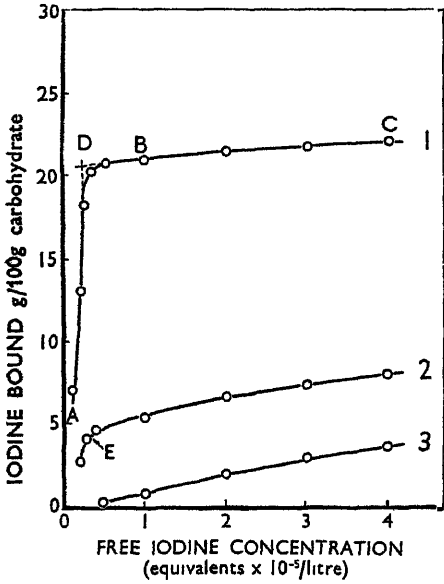

Fig 1

Curve (1). Pure potato amylose
Curve (2) Mixture of 22% amylose and 78% of amylopectin
Curve (3) Pure potato amylopectin (calculated from data for amylopectin containing 2·5% of amylose) Iodide concentration 0·05 N

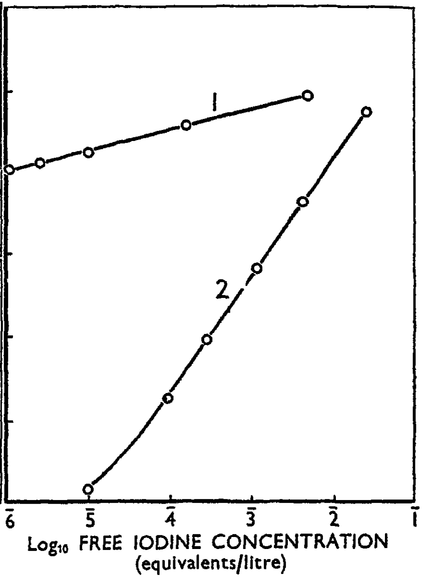

Fig 2

Curve (1) Pure potato amylose.
Curve (2) Pure potato amylopectin (calculated from data for amylopectin containing 2·5% of amylose) Iodide concentration 0·05 N

Pure or nearly pure amyloses are, however, adequately characterised by determining the amount of iodine bound at a definite concentration of free iodine which is sufficiently high for equilibrium between iodine and amylose to be practically instantaneous, but at which the amount of iodine absorbed by any amylopectin present is negligible; 10^{-5} N is a suitable iodine concentration. The pure amyloses of sago, maize, tapioca, and potato starches all absorb 21·0 per cent. of iodine in the presence of 10^{-5} N free iodine, 0·05 N. potassium iodide and 0·05 N potassium chloride at 25° C.[8] whereas the corresponding amylopectins absorb from 0·1 per cent. to 0·5 per cent. iodine. Throughout this series of papers the amount of iodine bound under these conditions will be referred to simply as the "iodine absorption" and for pure or nearly pure amyloses it is almost exactly equal (within 0·1 per cent.) to the value obtained by assuming that BC (curve 1, Fig. 1) is linear over the range

$C=10^{-5}$N to 5×10^{-5}N and extrapolating it to $C=0$, or to the point D. Thus the "iodine absorptions" quoted in this paper are comparable with those of other workers [1,10,12] By definition, "iodine absorption" is determined at 25° C, but the amount of iodine absorbed by pure amylose in the presence of 10^{-5}N iodine is not very sensitive to the temperature between 0° C. and 35°C (21 2 per cent. at 0° C., 20 0 per cent. at 35° C.).

For mixtures of amylose and amylopectin, the curves relating the percentage of iodine bound with the concentration of free iodine are intermediate in shape between the curves for the individual materials[1] and exhibit a well defined discontinuity (E, curve 2, Fig 1). When amylopectin predominates, the proportion of amylose in the mixture is most accurately determined by dividing the percentage of iodine bound at the point of discontinuity by the percentage of iodine bound by the pure amylose at the same concentration of free iodine. When the concentration of free iodine is low, the amounts of iodine bound by both amylose and amylopectin decrease with increasing temperature (Figs. 3 and 4) Over the range 0° to 40° C., the temperature coefficient for amylopectin is much the greater and the discontinuity in the iodine absorption curves for mixtures of amylose and amylopectin is the sharper the higher the temperature, and, when only a small amount of amylose is present, may disappear at lower temperatures (Fig. 3.) There appears to be no advantage in using a temperature higher than 25° C, but a lower temperature is undesirable. With mixtures containing more amylose than amylopectin there is no need to determine the point of discontinuity, the proportion of amylose is given with sufficient accuracy by the ratio of the percentage of iodine bound at a free iodine concentration of 10^{-5}N (determined by interpolation from three or four observations at free iodine concentrations between 0 5×10^{-5}N and 5×10^{-5}N) to the iodine absorption of pure amylose.

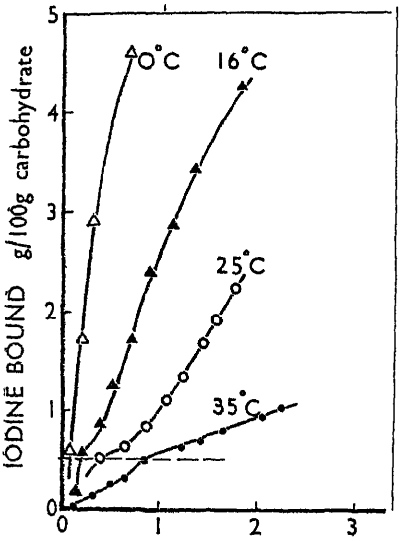

Fig 3
Potato amylopectin containing 2 5% amylose Iodide concentration 0 05N

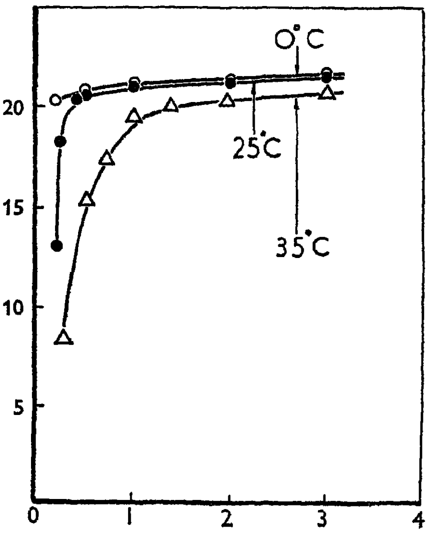

Fig 4
Pure potato amylose Iodide concentration 0 05N

The accuracy of the potentiometric method has been investigated by applying it to the analysis of mixtures of pure amylose with amylopectin, of known composition (Table I) The error is 1 per cent. or less when more than 50 per cent of amylose is present and increases as the amount of

Table I
Analysis of Mixtures of Amylose and Amylopectin

Potato amylose and Potato amylopectin			Tapioca amylose and Tapioca amylopectin		
Amylose in mixture %	Found %	Error %	Amylose in mixture %	Found %	Error %
3·1	3·4	10	2·3	2·0	15
19·7	20·0	1·5	7·5	7·1	5
47·8	47·2	1·3	29·9	29·4	1·7
64·7	64·6	0·2	39·4	39·2	0·5
			81·7	82·0	0·3

Table II

Starch	Amylose calculated from iodine absorptions of separate fractions %	Amylose by direct titrations %	Error %	Amylose from "Blue Value" %	Error %
Maize	28·5	26·5	8	25·4	10
Sago	26·3	26·9	2	24·4	7
Potato	22·1	21·3	3	23·2	5
Tapioca	18·0	18·4	2	17·8	1

amylose decreases. The amylose contents of sago, potato and tapioca starches (Table II) determined after dissolution in N-potassium hydroxide[9] are in excellent agreement with the values calculated from the amylose contents of the fractions separated after dispersing the starch by autoclaving or otherwise.[8] With maize starch, there is an appreciable discrepancy which is most probably related to the presence of about 0·1 per cent. of fatty acid which cannot be removed by extraction of the granular starch with methanol, but which is easily removed after dispersion of the starch in water.[12] Since the separated fractions are treated with good fat solvents (methanol or butanol) they do not contain fatty acid. It has been shown that addition of fatty acid to amylose reduces the amount of iodine it absorbs.[10,18]

2. COLORIMETRIC METHOD

Amylose can be determined colorimetrically because there is a large difference (about 1000A) between the wave-lengths of maximum absorption of the iodine complexes of amylose and amylopectin.[7] The maximum extinction coefficient for amylose is greater than that for amylopectin, especially when the concentration of free iodine is low [7] Colorimetric methods are more arbitrary than the potentiometric method because the extinction coefficients of the iodine complexes of both amylose and amylopectin vary with the concentration of free iodine, and, to some extent, with the variety of starch.[7] When the concentration of free iodine is fairly high, the influence of temperature can be neglected.

In the present paper attention is confined to one of the proposed methods, namely, Bourne and Peat's modification[5] of the method of Hassid and McCready [3] In this method, the test solutions contain 5 mg of carbohydrate, 10 mg of iodine, 100 mg. of potassium iodide and 20 mg. of sodium chloride in 500 ml. of water. If the carbohydrate is pure amylose, about 1 mg. of iodine will be absorbed. Thus the free iodine concentration may vary between 0·00014 N and 0·000155 N, which will entail a variation of not more than 1 per cent. in the extinction coefficient of the iodine complex. In Hassid's original method, a Klett-Summerson photo-electric colorimeter was used with a red filter, and the solution was placed in a 20 mm. cell. Peat used a "Spekker Absorptiometer" with a red filter and a 40 mm. cell; the results are reported as "Blue Values". "Blue Value" is defined as the optical density of a layer of solution 40 mm. thick, corrected for the optical density of the free iodine.

The "Blue Values" of pure amyloses (iodine absorption—21·0 per cent.) and nearly pure amylopectins have been determined. The amounts of amylose (1-2 per cent. for sago, potato and tapioca, 6 per cent. for maize) in the amylopectins were determined by potentiometric titration, and the "Blue Values" of the pure amylopectins were calculated from the "Blue Values" of the slightly impure materials, and the "Blue Values" of the corresponding pure amyloses. The "Blue Value" of pure amylopectin varies from 0·06 to 0·16, that of amylose from 1·26 to 1·48, according to the variety of the parent starch (Table III). The results for amylose were reproducible to within 1 per cent. Haworth[17] has reported a "Blue Value" of 0·02 for a fraction which remains in solution when a potato starch paste is treated with a mixture of thymol and cyclohexanol. The proportion of the total amylopectin which is present in this fraction is not stated. To check the accuracy of the method, mixtures containing known amounts of potato amylose and amylopectin have been analysed. The amylose contents of the mixtures could be calculated from the "Blue Values" with fair accuracy (Table IV) provided that a correction for the contribution of the amylopectin was applied. The amylose contents of the natural starches calculated in this way from their "Blue Values" (Table II) are in fair agreement with the values obtained by the potentiometric method.

Table III

Material (Pure)	Per cent. of total amylose or amylopectin in starch included in fraction examined	"Blue Value"
Sago amylose	95	1·48
Tapioca amylose	93	1·26
Potato amylose	93	1·41
Maize amylose	80	1·40
Sago amylopectin	95	0·06
Tapioca amylopectin	95	0·08
Potato amylopectin	95	0·16
Maize amylopectin	90	0·08

Table IV
Analysis of Mixtures of Amylose and Amylopectin

Amylose in mixture %	Amylose content calculated from "Blue Value" No correction for amylopectin		Amylose content calculated from "Blue Value" Correction for amylopectin applied	
	Result %	Error %	Result %	Error %
3·8	14·7	290	4·0	5
6·7	17·7	150	7·2	7·5
16·5	26·3	60	16·9	2·4
31·2	39·2	25	31·4	0·6
70·5	73·6	4	70·5	0·0

EXPERIMENTAL

Materials

The methods used to prepare pure amyloses and amylopectins have been described elsewhere.[8] The starches employed were good-quality commercial samples. Sago, tapioca and potato starches were washed with distilled water before use; maize starch was extracted with hot, 85 per cent. aqueous methanol for several hours in a Soxhlet apparatus to remove as much of the fatty acid as possible, then washed with distilled water.

The iodine solution used in potentiometric titrations was prepared from a solution 0·0100 N in iodine, 0·500 N in potassium iodide and 0·500 N in potassium chloride which had been standardised against potassium dichromate.

Preparation of Solutions for Potentiometric Titration

Amylopectins and granular starches were dissolved in N-potassium hydroxide[9] Dissolution was complete within 24 hours at 4° C Amyloses, in the form of the moist butanol-complexes, were dissolved in hot water saturated with butanol, and the butanol was removed by evaporation, fresh water being added as required. The amounts of carbohydrate in all the solutions were determined by wet-combustion with potassium dichromate and sulphuric acid[11,15] Since the result given by this method is slightly too low[15] (98 per cent of theory for starch, amylose, amylopectin and glucose) a correction was applied to make the results comparable with those of other workers who have relied on direct weighing

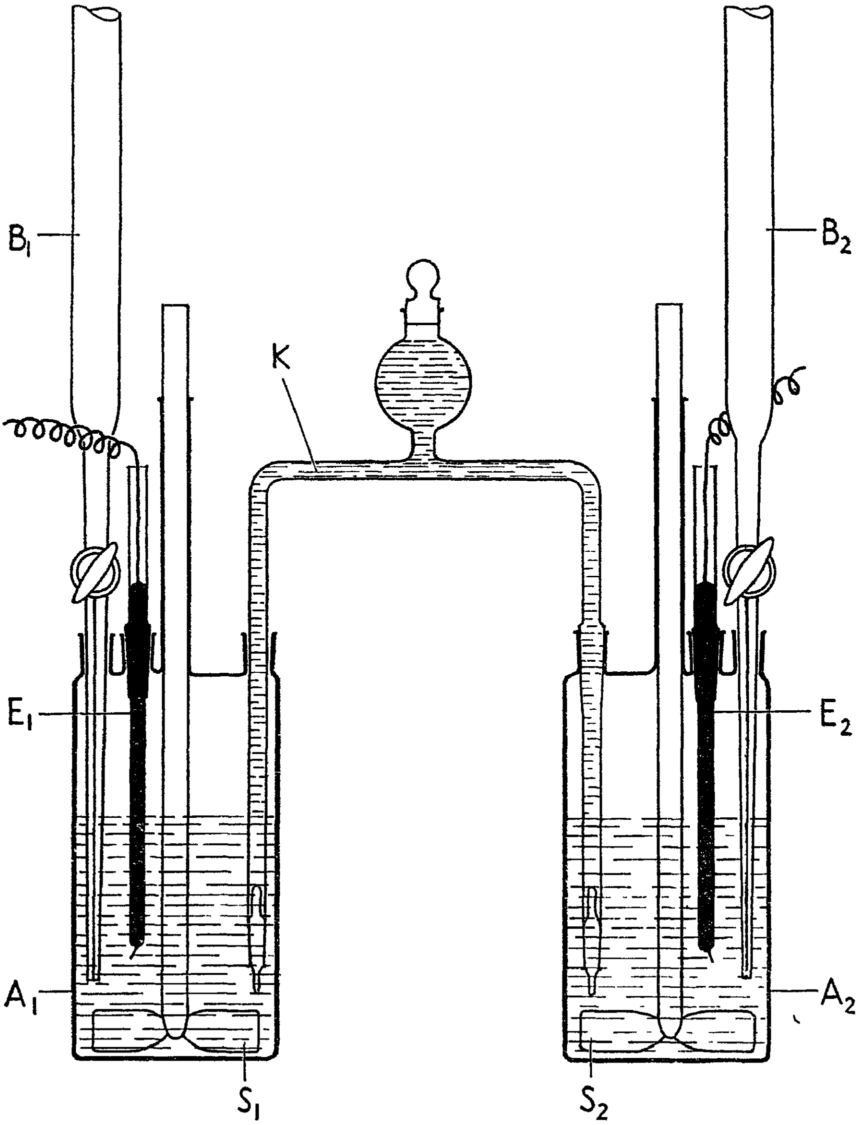

Fig 5

Potentiometric Titration

Essentially the method was the same as that used by Bates, French and Rundle,[1] but the actual measurement of potential differences has been avoided The apparatus (Fig 5) consisted of two similar resistance-glass vessels A_1, A_2 of about 150 ml capacity provided with platinum wire electrodes E_1, E_2, glass mechanical stirrers S_1, S_2, burettes B_1, B_2 and an all-glass bridge K[16] filled with saturated potassium chloride solution The vessels, mounted in a metal frame, were placed in a thermostat kept at 25° C. The electrodes were connected to a Cambridge D'Arsonval galvanometer (sensitivity 150 cm./micro-ampere, resistance 700 ohms) through a tapping key.

Fifteen ml of an alkaline carbohydrate solution containing from 0·04 to 0 20 g. amylose/100 ml. was neutralised with hydrochloric acid, after which 2·495 g of potassium iodide was added, the volume was made up to 100 ml., and the *pH* was adjusted to approximately 4·0 (yellow-green to Bromocresol Green) A portion (30 ml) of this solution was placed in one of the titration vessels and diluted with 60 ml of water. Ninety ml of 0·05 N solution of potassium iodide, 0·05 N in potassium chloride and adjusted to *pH* 4·0, was placed in the other vessel. A predetermined volume of a 0·001 N iodine solution was added to the test solution, and after equilibrium had been established (this required from less than one minute to ten minutes or more according to the concentration of free iodine) the same iodine solution was slowly added to the control solution until no current flowed through the galvanometer when the key was depressed. From the result the concentration of free iodine in the test solution was calculated. (Normally the effect of tri-iodide formation and absorption of iodide by amylose or amylopectin upon the free iodide concentration could be neglected The procedure employed when this could not be done will be described in Part III of this series of papers) The process was repeated until a sufficient number of points on the absorption curve had been obtained.

Colorimetry

The method employed differed from Peat's modification of the method of Hassid and McCready only in the means employed to dissolve the materials. Solutions of amylose were prepared directly from the butanol complexes without the use of alkali; amylopectins were dissolved in hot water, and granular starches were dissolved in normal sodium hydroxide at 5° C.

REFERENCES

[1] Bates, French and Rundle *J Amer Chem Soc*, 1943, 65, 143,

[2] Hassid and McCready *J Amer Chem Soc*, 1943, 65, 1154.

[3] Kerr and Trubell. *Paper Trade J*, 1943, 117, *TAPPI* Section, 161.

[4] Simerl and Browning *Ind Eng Chem* (*Anal Ed*), 1939, 11, 125

[5] Bourne and Peat *J Chem Soc*, 1945, 877.

[6] Lampitt, Fuller and Goldenberg *J Soc Chem Ind*, 1947, 66, 10

[7] Baldwin, Bear and Rundle *J Amer Chem Soc*, 1944, 66, 111

[8] Higginbotham and Morrison Succeeding Memoir (Part II of this series).

[9] Whistler and Hilbert. *J Amer Chem Soc*, 1945, 67, 1161.

[10] Schoch *J Amer Chem Soc*, 1944, 66, 1232

[11] Kerr *Arch Biochem*, 1945, 7, 377

[12] Whistler and Hilbert *J Amer Chem Soc*, 1944, 66, 1721

[13] Schoch *J Amer Chem Soc*, 1942, 64, 2954

[14] Birtwell and Ridge *Shirley Inst Mem*, 1928, 7, 37, or *J Text Inst*, 1928, 19, T341

[15] Richardson, Higginbotham and Farrow *Shirley Inst Mem*, 1935, 14, 63, or *J Text Inst*, 1936, 27, T131

[16] Irving and Smith *Ind Eng Chem* (*Anal Ed*), 1934, 6, 480

[17] Haworth, Peat and Sagrott *Nature*, 1946, 157, 19

[18] Mikus, Hixon and Rundle *J Amer Chem. Soc*, 1946, 68, 1115.

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12—THE FRACTIONATION OF STARCH

PART II—THE SEPARATION OF AMYLOSE AND AMYLOPECTIN

By R S. HIGGINBOTHAM and G. A. MORRISON

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Recent researches have firmly established the heterogeneous nature of starch and much progress has been made towards elucidating the structure of the two main constituents, amylose and amylopectin. The technique of separating these components has been greatly improved by the discovery that amylose can be preferentially precipitated from aqueous solutions of starch by certain organic compounds,[1] and several partial separations have been made in this way. (Table I.) Up to the present, however, a complete separation has not been achieved, and it is still not certain that starches contain only two sharply differentiated substances.

The investigation described in the present paper was commenced in order to determine whether sago, tapioca, potato and maize starches could be separated quantitatively into two fractions consisting solely of amylose and amylopectin. The "iodine absorption" of the fractions[2,3] has been used as the criterion of purity. The fractions which have been assumed to represent "pure" amylose and "pure" amylopectin may well be non-homogeneous in chemical structure as well as in molecular size and attempts to fractionate them further are still in progress. The highest published value for the "iodine absorption" of amylose is 20·6 per cent.[8] for a fraction representing about 15 per cent. of the total amylose in maize starch. By repeated crystallisation of impure amyloses from very dilute solutions in water saturated with butanol, a limiting value of 21·0 per cent. has been obtained for products including from 80 per cent. to 95 per cent. of the total amylose in the starches examined (Table II) and this figure is assumed to represent the value for pure, unfractionated amylose. Failure of other workers to obtain amylose of such high purity may be due to the use of too high a concentration during re-crystallisation This greatly reduces the efficiency of the process, as exemplified by the results in Table III.

The "iodine absorption" of pure amylopectins, calculated from the iodometric titration data for slightly impure samples, range from 0·1 per cent. to 0 5 per cent., according to the variety of the parent starch No means of purifying amylopectin has yet been discovered, so the conditions of the initial precipitation must be chosen to keep the amount of amylose in the non-precipitated fraction as small as possible. The claim that amylopectin can be freed from amylose by treatment with cellulose[2,9,10] has not been substantiated; scoured cotton cellulose, freed from fatty impurities by extraction with methanol, absorbs less than 0 10 per cent. of its weight of amylose, and the amount absorbed is not related simply to the amylose concentration (Table IV).

The claims of other workers to have purified amylopectin in this way are based mainly upon the observation that amylopectin containing a small amount of amylose no longer gives a blue coloration with a trace of iodine after treatment with sufficient "cotton wool" or filter paper. This is due to formation of a complex[11] between amylose and fatty impurities derived from the cellulosic material and not to absorption of amylose by the cellulose, for when the "purified" amylopectin is extracted with methanol to remove the fatty substances, it again gives a blue colour with iodine The material extracted from cotton "wool" or filter paper by methanol prevents the

Table I

Author	Starch	Method of dispersion	Precipitant	Per cent of starch precipitated	Amylose contents (%) (calculated from iodine absorptions except where otherwise stated)		Per cent of total amylose precipitated
					Precipitated fraction	Non-precipitated fraction	
Wilson, Schoch and Hudson[4]	Maize	Autoclaving	Butanol	22·8	76·0	8·1	75
	"	"	Butanol+*iso*-amyl alcohol	24·9	77·0	8·4	75
Schoch[5]	"	"	Pentasol	28·5	76·0	3·0	91
Whistler and Hilbert[6]	Maize	"	1-Nitropropane	27	69·0	—	66†
	"	"	2-Nitropropane	30	66·0	—	70†
	"	"	Nitroethane	22·5	75·0	—	59†
	Tapioca	"	1-Nitropropane	20·5	80·5	—	92‡
	Potato	"	"	26·5	84·5	—	99·5§
Haworth, Peat and Sagrott[7]	"	Boiling	Thymol	—	64–84*	1·5–6*	—
	"	"	Thymol + cyclohexanol	—	—	nil*	—

* From "Blue Values"
† Assuming 28·5% of amylose in original starch.
‡ " 18% " " " "
§ " 22% " " " "

Table II

Amylose from	"Iodine absorption" of product after N recrystallisations *						Fraction of total amylose included in final product
	N = 0	1	2	3	4	5	
Sago	18·7	20·5	20·9	21·0†			97
Tapioca	17·8	19·9	20·9	21·0†			93
Potato	18·5	21·0	21·0				93
Maize	14·5	18·1	19·0	20·1	21·0	21·0†	80

* Concentration during recrystallisation, 0·2 per cent unless otherwise stated.

† Recrystallised from 0·01 per cent solution

Table III

Material	Concentration during recrystallisation	"Iodine absorption"	
		Initial	After recrystallisation
Impure sago amylose	1·520	18·0	19·1
Impure sago amylose	0·237	17·8	20·5
Impure tapioca amylose	0·720	16·1	17·4
Impure tapioca amylose	0·307	16·2	19·1

Table IV

Amylose	Concentration of solution (gm./100 c.c.)	Gm. of amylose absorbed by 100 gm. of cellulose
Pure tapioca amylose (Iodine absorption 21·0%)	0·502	0·072
	0·243	0·048
	0·148	0·056
	0·072	0·039
Impure maize amylose (Iodine absorption 18·7%)	0·419	0·075
	0·195	0·060
	0·113	0·085
	0·057	0·051

formation of the blue coloration, but scoured cotton which has been extracted with methanol does not affect it. Since this work was completed Schoch[5] has reached the same conclusion.

In this investigation butanol[1], pyridine[6] and *iso*-amyl alcohol[4] have been employed as precipitants for amylose. At a suitable concentration pyridine gives similar results to butanol, but hot aqueous solutions of pyridine are better solvents for starch than hot water or hot water saturated with butanol. Amyl alcohol is less specific than butanol or pyridine; it will sometimes precipitate a larger proportion of the amylose, but the precipitates are always very difficult and sometimes impossible to purify.

It has been stated[1] that complete dispersion of a starch is essential to a complete separation of its components. There is, however, some ambiguity in the meaning of the word "dispersion". It is possible to determine when the coarser elements of granule structure in a starch paste have been broken down by diluting a sample to a concentration of about 0·3 per cent and centrifuging in a gravitational field of about 1000 g. Under these conditions all the coarser granule fragments are precipitated and an arbitrary value for the proportion of starch in "solution" can be determined. This method has been used to provide a measure of degree of dispersion in this investigation. However, even a paste which would be regarded as being completely dispersed by this criterion may still contain remnants of the original granule structure, including both components. Such fragments are extremely difficult to detect by any method at present available.

It is desirable that "complete dispersion" should be achieved in the mildest possible way to ensure that the starch has been chemically modified as little as possible. Sago, maize, tapioca and potato starches differ in the extent to which they swell and dissolve when heated with water or water saturated with butanol under the same conditions (Table V), and each, therefore, requires different treatment. The rate of dissolution is dependent on the speed of stirring as well as on the temperature. With moderately vigorous stirring, sago starch dissolved completely in water saturated with butanol within four to six hours at 90° C., potato and tapioca required one to two days under the same conditions, and the dissolution of maize starch was not complete after three days. All the starches dissolved within 2½ hours at 125° C. Maize starch dissolved completely at 90° in 30 per cent (the optimum concentration) aqueous pyridine within 24 hours, or within 2 hours at 120° C.

Table V

Starch concentration, 2%, Stirring speed, 500 r p m., Temperature, 90°C

Starch	Solvent	Time of heating (hours) Per cent Starch dissolved 1	2	4	6	10	24	53	72
Sago	Water saturated with butanol	96	97·5	99	100				
Potato	,, ,,	73	82	93	—	98·5	99·5	100	
Tapioca	,, ,,	88	95	99	99·5	99·5	100		
Maize	,, ,,	69	77	82	85	88	—	—	93
Maize	30% aqueous pyridine	91	94·5	95·5	97	99·5	100		

To detect any chemical modification of the starches which might have occurred during the separations, the intrinsic viscosities of the triacetates of the pure amyloses and amylopectins and, where possible, of the parent starches, have been determined. This is considered to be more reliable than measurements of reducing power or alkali-labile value. The possible solvents for viscosity measurements with substantially unmodified amylose and amylopectin triacetates are chloroform, tetrachlorethane, dichlorethane, nitromethane, nitroethane and 1-nitropropane. Tetrachlorethane is unstable, and the commercial product is a mixture of isomers which are troublesome to separate. Dichlorethane is not a powerful solvent, and is also unstable. Chloroform is inconvenient because of its high volatility, and does not completely dissolve all amylose triacetates. Amylose triacetates dissolve completely in the nitroparaffins only at temperatures above 50° C., but once prepared the solutions are quite stable and their viscosities at 25° C. are unchanged after storage for 10 days at 4° C (at this temperature a precipitate or gel is formed which disperses again on warming to 25°) or one hour at 95° C. Amylopectin triacetates usually dissolve completely at the ordinary temperature. Nitroethane was used for the measurements reported in this paper. In most cases η_{sp}/c plotted against either c or η_{sp} was linear over the range examined, and the values of the intrinsic viscosity $[\eta]$ determined by extrapolation of either curve were identical. Values of the constant k', in Huggin's equation[15] are reported. Since the solutions exhibited anomalous flow even at the lowest concentration the values of $[\eta]$ are dependent to some extent on the dimensions of the viscometer.

Of the starches examined, sago is most easily separated into its components (Table VI). When the starch was heated with water saturated with butanol for 2½ hours at 90° C. (97 to 98 per cent. of the starch dissolved), 96 to 98 per cent. of the total amylose was precipitated on cooling and could be purified without appreciable loss, except for an unavoidable random loss inherent in the mechanical manipulations. That fraction of the amylopectin which was precipitated initially along with the amylose could be recovered from the mother liquors from the recrystallisations. The amount of amylose which can be separated is not increased when the starch is dispersed by more drastic methods, namely, heating for 6 hours at 90° C. (100 per cent. starch dissolved) or for $2\frac{1}{2}$ hours at 125° C (100 per cent dissolved) with water saturated with butanol

Table VI

SOLVENT—Water saturated with butanol STARCH—Sago (Amylose content, 26 3 per cent)

Conditions of dispersion	Time (hours)	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$	6	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$
	Temperature (°C)	90	90	90	90	90	125	125	125
Per cent amylose in precipitated fraction		96	99	96 5	98	97 5	92 5	95·5	95 5
Amylose content of precipitated fraction		89 0	—	—	—	87 5	86 0	85 0	89 5
Per cent total amylopectin in non-precipitated fraction		95 7	95	96	95	91 5	92 5	96	94
Amylose content of non-precipitated fraction		1 6	0 7	1 4	1 0	1 0	2 8	1 6	1 9
Per cent total amylose isolated "pure" after N recrystallisations. .		95 5	97 5	96 0	97 0	—	92 0	94 5	93 5
Iodine absorption of amylose after N recrystallisations		21 2	21 2	21 2	21 0	—	21 1	21 0	21 1
N		2	2	2	2	—	3	2	2
Per cent. total amylopectin separated from mother liquors after crystallisation of amylose .		3 6	5	4	5	—	4 7	3 2	2 6
Amylose content of amylopectin from mother liquors		0 8	6 0	2 0	5 0	—	3 3	4 6	18 1
Viscosity results: Amylose triacetate	$[\eta]$	1 80	1 82	1 90	1 78	—	1 76	1 65	1 47
	k'	0 17	0 25	0 26	0 23	—	0 24	0 27	0 27
Viscosity results: Amylopectin triacetate	$[\eta]$	1 09	1 04	1 10	1 06	1 02	—	—	0·94
	k'	0 52	0 61	0 56	0 69	0 78	—	—	0 49

The triacetates of the fractions isolated in duplicate experiments after dispersion of the starch at 90° C. had nearly identical intrinsic viscosities The intrinsic viscosity of the triacetate of the original starch was 1·46, and the weighted means for the separated components ranged from 1 25 to 1 32, suggesting that very slight chemical modification may have occurred. The triacetates of the amyloses isolated from autoclaved pastes were less uniform in intrinsic viscosity, and two of them were considerably modified Therefore, with sago, autoclaving is both unnecessary and undesirable

With tapioca and potato starches the mild method of dispersion successfully employed with sago did not result in a complete separation of the components (Table VII). The proportions of the starches which dissolved were respectively 95 per cent. and 85 per cent. The most striking feature of the results is that, although the proportion of the total amylose precipitated initially is not much lower than when conditions giving complete dispersion are used, the losses during recrystallisation are considerable This suggests that granule fragments containing both amylose and amylopectin which are present in the initial precipitate are broken down sufficiently during recrystallisation to prevent their precipitation by the centrifuge, but that sufficient amylopectin remains attached to the amylose to prevent its separation as butanol complex

When these starches were completely dispersed in water saturated with butanol by suitable conditions of heating, an almost complete separation of the components was effected Heating for 40 hours at 90° C entailed more chemical modification of potato amylopectin (Table VII) and less modification of potato amylose than heating for 2½ hours at 125° C. An alternative method of producing complete dispersion which does not involve prolonged heating or autoclaving is to pass a fairly concentrated (5-10 per cent) paste which has been heated for a short time at 90° C. through a homogeniser. Butanol or pyridine may be used as the amylose precipitant, the optimum concentration of the latter being about 15 per cent by volume for these starches A very complete separation was achieved by this means (Table VIII), and the fractions isolated from potato starch were little, if any, more modified than when other methods of dispersion were employed With tapioca, however, homogenising caused considerable modification of the amylose Pyridine gives a less pure and more bulky initial precipitate than butanol.

The triacetate of potato starch was almost insoluble and that of tapioca starch only partially soluble (95 per cent) in nitroethane even at 90° C., although the triacetates of all fractions separated from the starches were readily soluble on warming This suggests that the granular starches may contain highly ordered regions which persist in the triacetates and resist the action of the solvent, or that they contain cross-linkages which are broken when the granules are dispersed in hot water, but remain intact during acetylation Slight chemical modification of the components during their separation would also increase the solubility of their triacetates. Since sago triacetate is readily and completely soluble, it is unnecessary to postulate the existence of any form of cross linking

When maize starch was heated with water saturated with butanol for 2½ hours at 90° C., 80 per cent of the starch was dissolved and 83 per cent. of the total amylose was precipitated on cooling. The purity of the precipitate was very low and the loss of amylose during its purification heavy, owing to the presence of undispersed starch. Only 72 per cent. of the total amylose could be isolated at a purity of 98 per cent When the starch was heated for 2½ hours at 90° C. with 15 per cent. pyridine, 90 per cent. was dissolved, the precipitate formed on cooling contained a higher proportion of amylose than in the previous experiment, the loss during purification was smaller, and the final yield of pure amylose greater. (Table IX.) In accordance with expectation, more complete dispersion gave a better separation. Complete dispersion of the starch by a variety of methods (Table IX) did not, however, give any further improvement. In general, not more than 87 per cent. of the total amylose was precipitated initially and not more than 80 per cent. could be separated pure. In one experiment in which a homo-

Table VII

SOLVENT—Water saturated with butanol. AMYLOSE CONTENTS. Tapioca starch, 18·0 per cent; Potato starch, 22·1 per cent.

Starch		Tapioca	Potato	Potato	Potato	Tapioca	Tapioca
Conditions of dispersion	Time (hours)	2½	2½	44	2½	2½	2½
	Temperature (°C)	90	90	90	125	125	125
Per cent total amylose in precipitated fraction		95·0	91·0	93·5	94·5	96·0	93·5
Amylose content of precipitated fraction		78·0	82·0	91·0	88·5	77·0	77·0
Per cent total amylopectin in non-precipitated fraction		94·0	95·5	95·5	96·5	93·5	94·0
Amylose content of non-precipitated fraction		1·1	2·8	1·8	1·6	1·1	1·4
Per cent total amylose isolated "pure" after N recrystallisations		87·0	86·5	93·0	94·5	93·5	92·5
Iodine absorption of amylose after N recrystallisations		19·8	20·0	21·1	21·0	20·8	21·0
N		3	1	1	1	4	4
Per cent total amylopectin separated from mother liquors after crystallisation of amylose		5·3	5·4	3·5	3·3	5·7	4·2
Amylose content of amylopectin from mother liquors		25·5	19·5	4·6	0·2	5·5	2·8
Viscosity results: Amylose triacetate	[η]	2·28	2·04	1·97	1·80	2·60	3·00
	k'	0·27	0·27	0·30	0·26	0·22	0·23
Viscosity results: Amylopectin triacetate	[η]	1·56	1·64	1·31	1·66	1·40	1·44
	k'	0·60	0·52	0·84	0·55	0·66	0·76

Table VIII

Starches dispersed by homogenising.

Starch		Potato	Potato	Tapioca	Tapioca
Precipitant		Butanol	15% Pyridine	Butanol	15% Pyridine
Per cent total amylose in precipitated fraction		94·0	98·0	98·0	99·5
Amylose content of precipitated fraction		81·5	69·0	85·0	69·0
Per cent total amylopectin in non-precipitated fraction		94·0	88·0	96·0	90·5
Amylose content of non-precipitated fraction		2·0	0·9	0·5	0·1
Per cent total amylose isolated "pure" after N recrystallisations		94·0	97·0	98·0	99·0
Iodine absorption of amylose after N recrystallisations		21·0	21·1	21·0	20·8
N		1	2	2	2
Per cent total amylopectin separated from mother liquors after crystallisation of amylose		4·0	9·3	3·3	8·6
Amylose content of amylopectin from mother liquors		0·0	1·4	0·5	1·4
Viscosity results: Amylose triacetate	[η]	2·09	1·57	1·28	1·43
	k'	0·38	0·30	0·37	0·47
Viscosity results: Amylopectin triacetate	[η]	1·40	1·38	1·00	1·23
	k'	0·47	0·54	0·60	0·65

Table IX. Maize Starch : Amylose Content 28·5%

Conditions of dispersion				Precipitant	Amylose content		% Total amylopectin in non-ppt'd fraction	% Total amylose		Iodine absorption after N recrystallisations	% Total Amylopectin sep from mother liquors after recrystallisation	Amylose content of Amylopectin from mother liquors	N	Viscosity results			
Temp. ° C.	Time, hours	Solvent	% Starch dissolved		Ppt'd fraction	Non-ppt'd fraction		Ppt'd initially	Isolated after N recrystallisations					Amylose triacetate		Amylopectin triacetate	
														[η]	k′	[η]	k′
90	2½	Water saturated with butanol	80	Butanol . .	63·0	7·8	80·0	83·3	71·7	20·8	13·2	10·0	5	1·12	0·33	1·00	0·57
90	70	Water saturated with butanol	93	Butanol.	82·0	8·8	—	75·2	—	—	—	—	—	—	—	—	—
90	2½	15% aqueous pyridine	90	15% pyridine ..	70·0	6·6	85·0	85·2	79·5	21·1	8·0	16·7	4	1·34	0·25	1·33	0·76
90	24	30% aqueous pyridine	100	15% pyridine ...	76·0	8·5	—	80·3	—	—	—	—	—	—	—	—	—
120	2	30% aqueous pyridine	100	15% pyridine ..	76·0	7·7	—	81	—	—	—	—	—	—	—	—	—
90	½	20% aqueous pyridine (Paste homogenised)	100	15% pyridine saturated with butanol	77·0	7·0	90·0	83	74·0	21·1	8·0	12·0	4	1·15	0·24	1·19	0·54
90	½	20% aqueous pyridine (Paste homogenised)	100	20% pyridine saturated with butanol	32·0	0·0	20·0	100	—	—	—	—	—	—	—	—	—
125	2½	Water saturated with butanol	100	Butanol	77·5	8·9	92·0	76·0	—	—	—	—	—	—	—	—	—
125	2½	Water saturated with butanol	100	Butanol + *iso*-amyl alcohol	58·0	6·3	79·0	87·0	83·0	20·7	—	—	5	1·03	0·34	1·28	0·59
4	72	N-KOH . .	100	15% pyridine ..	—	5·7	—	86·0	—	—	—	—	—	—	—	—	—

genised paste of maize starch in 20 per cent pyridine was saturated with butanol, the whole of the amylose precipitated on cooling, but 80 per cent. of the amylopectin was carried down with it. About 76 per cent. of the amylose was precipitated when an autoclaved paste of the starch in water saturated with butanol was allowed to cool. Addition of 5 per cent. of *iso*-amyl alcohol to the hot paste increased the amount of amylose precipitated on cooling to 87 per cent., but most of the additional material was lost to the mother liquor when the precipitate was recrystallised.

The triacetate of maize starch does not dissolve completely in nitroethane, though the triacetates of the separated components were all readily soluble

These results suggest that even when the dispersion of maize starch appears to be complete, aggregates containing both amylose and amylopectin are present which probably include about 20 per cent. of the total amylose and 80 per cent of the amylopectin. The nature of the bonds which cause these aggregates is at present obscure, but most probably ordinary valence bonds are involved, since hydrogen bonds or van der Waals attractions would presumably be broken by such dispersing agents as aqueous pyridine at 120° C. or N-KOH solution.

Maize thus occupies a unique position among the four starches examined Since an absolutely quantitative separation of the components of sago, tapioca and potato starches has not been achieved, these also may contain aggregates of the kind postulated for maize, but the proportion of the total amylose bound in such aggregates cannot exceed 3 per cent for sago and potato starches or 6 per cent, for tapioca starch

EXPERIMENTAL

Materials

The starches were good quality commercial samples. The sago, potato and tapioca starches were washed thoroughly with distilled water before use. Maize starch was extracted for 36 hours with 85 per cent. methanol in a hot-jacketed Soxhlet apparatus to remove lipoid impurities. The *pH* of a 2 per cent. aqueous paste of the purified materials was 6·5

Butanol (commercial) was purified by distillation with a column after addition of 15 gm. of sodium hydroxide per litre to resinify aldehyde impurities and combine with any free acid.

Pyridine was shaken with stick caustic soda and distilled with a column.

Iso-amyl alcohol, of the grade used for milk testing, was used without any attempt at purification.

Nitroethane, supplied by Messrs. Imperial Chemical Industries Ltd , was freed from acid by shaking with 10 per cent sodium carbonate, washed with dilute sodium chloride solution, dried over fused calcium chloride, and distilled under reduced pressure with a column. B R 54·5-55 0° at 95 mm. of mercury

Preparation of Pastes

In general, pastes were prepared by stirring a mixture of starch (200 g) and solvent (10 litres) at 500 r.p.m in a Pyrex flask fitted with a reflux condenser and immersed in a thermostat. When 30 per cent pyridine was the solvent, the starch concentration was twice as great and the paste was diluted with an equal volume of hot water before cooling Pastes for autoclaving were first heated and stirred for 2 hours at 90° C. Pastes for homogenising were prepared by stirring a mixture of starch (200 g) and solvent (3 litres) at 90° C. for 30 minutes. The homogeniser was fitted with a steam jacket to prevent undue cooling of the paste during the treatment. The homogenised paste was diluted to the desired composition with butanol or pyridine, and the final starch concentration was 2 per cent. Maize starch was dispersed in potassium hydroxide (Table X) as follows The starch (20 g) suspended in water (150 ml) was added to a quantity (500 ml.) of

1 3 N potassium hydroxide solution with mechanical stirring, and the resultant paste was kept at 5° C. for 3 days Pyridine (60 per cent., 250 ml.) was added (to prevent retrogradation after neutralisation) followed by a sufficient amount (100 ml.) of 6·5 N acetic acid The solution was then heated to 80° C.

Determination of Percentage of Starch "Dissolved"

A quantity (10 ml.) of the hot paste (starch concentration 2 per cent.) was diluted with cold distilled water (50 ml). A portion (15 ml.) of the diluted solution was placed in a graduated tube and centrifuged for 30 minutes in a gravitational field of about 1000 **g**. The starch concentrations of the uncentrifuged solution and the supernatant liquor (c_1 and c_2 respectively) were determined by wet combustion with dichromate and sulphuric acid[12,13] after boiling off any butanol or pyridine. If v is the volume of the centrifuge tube occupied by the precipitate, the percentage of starch dissolved is taken to be $100(15\text{-}v)c_2/15c_1$. This value will be too low if the precipitate occupies an appreciable volume because of the entrainment of dissolved starch.

Separation of Amylose and Amylopectin

The pastes were allowed to cool slowly to room temperature, and after 3 or 4 days the precipitate of impure amylose was separated by means of a supercentrifuge running at 35,000 r.p m. The weights of carbohydrate in the original paste and in the precipitated and non-precipitated portions were determined by drying weighed samples at 110° C. The weight of the precipitated fraction was determined before removal from the centrifuge bowl. The material balance was generally correct to within 1 per cent. The amylose contents of the fractions were determined from their "iodine absorptions" [3]

The non-precipitated fractions were evaporated under diminished pressure (5 cm. mercury) to about one-tenth of their original volume, and sprayed into methanol containing a little sodium acetate. The precipitates were ground with dry methanol, washed with ether, and dried at a low temperature. The products are referred to in the text as "amylopectin" irrespective of whether or not they contain traces of amylose.

Pure amylose was isolated from the precipitated fractions by repeated recrystallisation. Twenty g. of impure amylose (in the form of the moist complex with butanol or pyridine) was suspended in a mixture of butanol (100 ml.) and water (900 ml) and stirred at 90° C for 1 hour. The clear solution was poured through a fine wire gauze into 8000 ml of water and 1000 ml. of butanol at 90° C., the mixture was stirred for a short time and then allowed to cool. The fractions were separated and analysed as before. Pure amyloses were stored as butanol complexes.

Determination of the Amount of Amylose adsorbed by Pure Cellulose

Fifteen ml. of amylose solution was added to 2 g. of thoroughly scoured cotton which had been extracted with hot 85 per cent. methanol. The mixture was stirred occasionally during 1½ hours and the liquid was separated by centrifuging. The concentration of amylose in solution was determined before and after this treatment by wet combustion with dichromate and sulphuric acid.[12,13]

Preparation of Triacetates

Amylose triacetate was prepared directly from the highly reactive butanol complex. A quantity of the complex containing 7·5 g. of amylose, dehydrated as far as possible by repeated treatments with dry butanol, was suspended in pyridine (100 ml.) by vigorous mechanical stirring. The suspension was then centrifuged and the precipitate washed twice with fresh pyridine to displace all the butanol. The washed precipitate was suspended in a mixture of 75 ml. pyridine and 75 ml. of acetic anhydride. A clear solution was produced within 12 hours at room temperature, but three days were allowed to complete the reaction. After removal of any foreign matter (cellulose fibre, dirt, etc.) by filtration through sintered glass or by centrifuging, the solution was poured into a mixture of ice and water. The triacetate was precipitated as a fibrous mass which was washed with distilled water till free from acid, and dried at a low temperature.

Amylopectins could be completely acetylated only after pre-swelling in aqueous pyridine, and great care was needed to ensure uniform dispersion. A quantity (5 g.) of amylopectin (ground in a mortar to pass a 100-mesh sieve) was suspended in dry pyridine (35 ml.), and a mixture of water (10 ml.) and pyridine (21·5 ml.) was added slowly with constant shaking. The clear, uniform, viscous dispersion which formed was kept for 2 hours and acetic anhydride (100 ml.) was then added very slowly, the mixture being shaken after each addition and well cooled. After three days at room temperature the triacetate was recovered as described above. Although the conditions of acetylation were somewhat less mild than for amylose owing to the unavoidable presence of a little more acetic acid (from the added water) it is unlikely that any modification occurred, for the reaction was very rapid and the *pH* of the reaction mixture remained above 5. Attempts to acetylate pre-swollen amylopectin after removing the water as a pyridine-water azeotrope[14] were unsuccessful.

It proved possible to acetylate potato starch after swelling at 4° C. with 85 per cent. pyridine,[14] but sago, maize and tapioca starches did not swell sufficiently under these conditions. All of the starches were sufficiently swollen after heating to 90° with 70 per cent. pyridine. A mixture of air-dry starch (5 g.; passed through a 100-mesh sieve), pyridine (35 ml.) and water (15 ml.) was heated to 90° during 20 minutes (with shaking), cooled, and mixed with a further quantity (50 ml.) of pyridine. Acetic anhydride (150 ml.) was added slowly with vigorous shaking and good cooling. The mixture was shaken overnight and stored for 5 days at room temperature, when a gel was formed which could be liquefied to some extent by shaking. The triacetate was isolated as before except that filtration was neither necessary nor practicable.

Determination of Intrinsic Viscosities

A quantity (0·80 g.) of triacetate (dried *in vacuo* over phosphorus pentoxide for two days at room temperature) was weighed accurately into a glass tube fitted with a ground-in stopper and nitroethane (20 ml.) was added. The mixture was shaken for one hour at room temperature and then heated for 20 minutes at 60° C. The tube and contents were weighed before and after heating and allowance was made for any loss of solvent by evaporation. The cooled solutions were passed under pressure through a G-4 sintered glass filter. Dilutions were made as required. Measurements of viscosity were made in a viscometer (B.S.S. No. 1) of the U-tube type adapted for pipette filling,[16] in a thermostat at 25° ± ·01° C. The important dimensions were as follows:—

Capillary	length .	10 cm.
	internal diameter .	0·05 cm.
Bulb capacity ..		5·0 ml.
Mean head		11·5 cm.

Concentrations are expressed as g./100 ml. solution. The flow time of the solvent was about 148 secs. and was constant to within ±0·15 per cent. over a period of some months. A kinetic energy correction was applied where necessary.

"Iodine absorptions" were determined by Miss M. M. Bridges, the preparation of the triacetates and the measurements of their viscosities were carried out by Miss J. Gosling, and some of the separations were made by Mr. D. Goodison.

REFERENCES

Schoch. *J Amer Chem Soc*, 1942, **64**, 2957.
[2] Bates, French and Rundle. *J Amer. Chem Soc*, 1943, **65**, 143.
[3] Higginbotham and Morrison Part I of this series.
[4] Wilson, Schoch and Hudson. *J Amer Chem Soc*, 1943, **65**, 1380
[5] Schoch " Advances in Carbohydrate Chemistry," Vol 1 New York, 1945
[6] Whistler and Hilbert *J. Amer. Chem Soc.*, 1945, **67**, 1161
[7] Haworth, Peat and Sagrott *Nature*, 1946, **157**, 19
[8] Kerr. " Chemistry and Industry of Starch," New York, 1944.
[9] Pacsu and Mullen *J. Amer. Chem. Soc*, 1941, **63**, 1168
[10] Tanret. *Bull Soc. Chim*, 1915, 83
[11] Schoch. *J. Amer. Chem Soc*, 1944, **66**, 1232.
[12] Birtwell and Ridge *Shirley Inst. Mem*, 1928, **7**, 37, or *J Textile Inst*, 1928, **19**, T341.
[13] Richardson, Higginbotham and Farrow. *Shirley Inst Mem*, 1935, **14**, 63, or *J. Textile Inst.*, 1936, **27**, T131
[14] Richardson and Higginbotham. *J. Soc Chem. Ind.*, 1938, **57**, 234
[15] Huggins. *J. Amer Chem. Soc*, 1942, **64**, 2717.
[16] British Standards Institution " Determination of Viscosities of Liquids in Absolute (C.G.S) Units," London, 1937, p. 16.

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13—MEASUREMENT OF MODULUS AND DAMPING CAPACITY IN TORSION AND IN BENDING FOR WOOL AND OTHER TEXTILE FIBRES

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ABSTRACT

A method is described for the determination of the damping capacity for torsion of fibres. The damping capacity is obtained from the decay of torsional oscillations of a small disc suspended from a fibre

A method for the determination of Young's modulus for bending of short fibres is also described. Young's modulus is calculated in terms of length, diameter, density and fundamental frequency of transverse vibrations when excited to resonance by either an electromagnet or a sound field The damping capacity of the same fibre is determined from the sharpness of resonance.

Results obtained by the two methods of measurement of damping capacity are in good agreement for homogeneous fibres For fibres having a heterogeneous structure such as wool, the damping capacity for bending is not necessarily the same as the value for torsion.

INTRODUCTION

Young's modulus of wool and other fibres has been measured by various investigators.[1] In all cases the fibre was stretched along its length and Young's modulus determined from the static stress strain relation below the elastic limit.

Forces in fibrous materials, however, produce bending as well as stretching. For homogeneous substances the Young's moduli obtained by bending and stretching are equal, but this cannot be assumed to be the case for most textile fibres. Carlene[2] employed a static method of measuring the modulus by bending, but his method was not suitable for fibres of diameter smaller than 0·3 mm Yousef[3] measured the frequency of flexural oscillations of horsehair and other materials in filament form when tapped. His method is also unsuitable for textile fibres.

In the present paper a simple and accurate method of determining Young's modulus by transverse vibrations of fine fibres is described. Furthermore, the effects of temperature, humidity, chemical treatment, *etc* , on the modulus can be studied very conveniently

Up to the present attention has been paid only to hysteresis losses occurring during extension of textile fibres, and for this purpose fibres have been stretched far beyond the elastic limit. In the case of bending it is doubtful whether in practice the elastic limit is ever exceeded and a study of the internal friction giving rise to hysteresis losses within the elastic limit seems to be imperative. Apart from the structural properties of a fabric, it is possible that the resistance against fatigue of a fabric may depend very largely on the damping capacity or internal friction of the fibres and may be greater the higher the damping capacity, but whether this is the case or otherwise has still to be investigated.

In this paper two methods for measuring the damping capacity of fibres are described.

Analysis of the vibrating systems encountered is often simplified by the use of electrical analogies. Although not generally realized, the electrical circuit is the most commonly used vibrating system By suitable substitution of coefficients in the differential equations describing the movement, the solutions in A.C electrical theory can be used to good purpose in mechanical vibrating systems

DAMPING CAPACITY

Most materials exhibit appreciable plastic strain under cyclic stresses well within the "elastic limit". This plastic strain, which accompanies the elastic strain, is responsible for the so-called mechanical hysteresis loop, the area of which represents the energy converted into heat during one cycle It is this conversion into heat or absorption of kinetic energy that damps out the resonant vibrations of elastic bodies.

The "damping capacity", defined by O Foppl[4] as the non-dimensional ratio ψ, obtained by dividing the area of the hysteresis loop by the strain energy stored in the extreme position of the cycle, depends on the ratio of the plastic to the elastic strain, and is an important physical property of materials to be used under alternating stresses Damping in any material depends on the amplitude of swing, the temperature of the specimen and on the number of stress cycles completed, but it does not become exhausted in time and is no indication of impending fatigue failure

Thus, damping capacity is a property of genuine practical importance in judging materials and can be relied on to the same extent as can the breaking point of the steel of a machine part.

According to Foppl a material of high damping capacity is superior to one of low damping capacity for the following reasons:

(*a*) According to elastic theory, there are severe local concentrations of stress at certain spots such as flaws, surface scratches, *etc.*, which may reach values from twice to five times the surrounding stress Consequently fatigue cracks are particularly prone to start from surface blemishes The effect of plastic strain is to lessen the intensity of a peak stress by spreading it over a wide area On this account, the danger of starting a fatigue crack is diminished.

(*b*) When a machine part is thrown into resonant vibration by a periodic exciting force, the amplitude of swing is held in check by damping resulting from the conversion of kinetic energy into heat This means that if a material possesses high damping capacity it will not be so severely stressed Resistance to fatigue failure depends essentially on the area of the hysteresis loop, *i e*, on the damping capacity of the material.

Overhead cables stretched by a given force may fail by fatigue due to resonant vibrations excited by cross winds. It is found that copper possessing strong damping properties is less likely to fail than light-metal alloys possessing greater tensile and fatigue strengths than copper

For the same reason mine cables should be made of steel with a high damping capacity to absorb standing and shock waves. Similar conditions apply to the wings of aeroplanes, propellers of aeroplanes, crankshafts of internal combustion engines, blading of steam turbines, *etc.*

Very often ropes and belts are made of organic fibrous materials The useful life of such ropes and belts will depend on the damping capacity of the fibres of which they are made Similarly the strength and resistance to fatigue of fabrics depend on the damping capacity of its fibres The superiority as regards resistance to bending fracture of wool and nylon[5] over most of the artificial fibres may be due to the fact that their damping capacity is high compared with the damping capacity of the other fibres It is, therefore, of the utmost importance to be able to measure the damping capacity of fibres.

DETERMINATION OF THE MODULUS OF RIGIDITY AND DAMPING CAPACITY FOR TORSIONAL STRAIN OF FIBRES

The modulus of rigidity[6] and damping capacity of fibres can conveniently be measured by measuring the period and decay of damped oscillations of a small disc of known dimensions and weight suspended from a fibre of known length and diameter.

There is no simple law which governs the variation of frictional forces in the fibre and forces due to the disc moving through the air offering resistance to its motion. Experiments indicate that the law of resistance changes with the velocity of oscillation of the disc. For small velocities, however, it is found that the retarding force, due to internal and air friction is proportional to velocity.

It is found that if we plot the amplitude of successive swings on a logarithmic scale *vs* number of swings, then a straight line can be drawn through all points as long as the amplitude of oscillation is small (see Fig. 2). The ratio of one maximum to the next is given by

$$\frac{\theta_1}{\theta_2} = \frac{\theta_2}{\theta_3} = \frac{\theta_3}{\theta_4} \ldots\ldots \ldots\ldots = e^{\delta}$$

$$i.e.\ \delta = \text{Log}_e \frac{\theta_1}{\theta_2}, \qquad \ldots (1)$$

where δ is known as the logarithmic decrement and is readily obtained from the decay curves of Fig. 2 using the formula

$$\delta = \frac{2{\cdot}3}{n} \text{Log}_{10} \frac{\theta_o}{\theta_n}, \qquad \ldots (2)$$

n being the number of swings and $\frac{\theta_o}{\theta_n}$ the ratio of the amplitude of a certain swing to that of another swing n cycles later.

The damping capacity ψ defined as the non-dimensional ratio of the energy dissipated per cycle to the maximum strain energy is given by

$$\psi = \frac{\theta_1^2 - \theta_2^2}{\theta_1^2} = 1 - \left(\frac{\theta_2}{\theta_1}\right)^2 = 1 - e^{-2\delta} \qquad \ldots (3)$$

where θ_1 and θ_2 are amplitudes of successive swings

Values of ψ determined from samples of different materials are given in Table 2. The tests were conducted in a vacuum in order to eliminate air friction losses. It was found, however, that for ordinary textile fibres, the air friction losses are negligible compared with internal losses and tests can be conducted under atmospheric pressure.

If it is required to determine ψ for low loss materials such as quartz, glass, *etc.*, it will be necessary to make a small correction for air friction losses. The air friction losses for a particular disc can be determined from the decay curves in air and in vacuum of the disc suspended from a quartz fibre. The decay curves of a silvered glass disc 1·07 cm diameter and 0·0559 cm. thick, weighing 0·1185 grams, suspended from a quartz fibre 7 12 cm. long and 0·0032 cm. diameter are given in Fig. 3.

The disc is set into oscillation by suddenly removing a strong magnetic field from the vicinity of the disc Either a strong permanent magnet which produces a couple on the disc may be pulled away or the current through an electromagnet may be switched off. Even though the disc is made of glass the couple produced by the magnetic field will be enough to make it swing

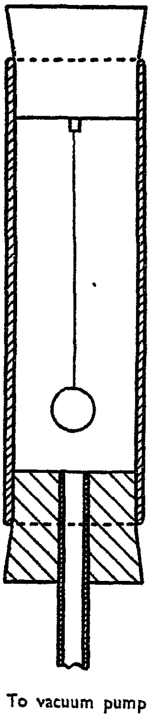

Fig 1
Apparatus for the determination of modulus of rigidity and damping capacity for torsion of a fibre

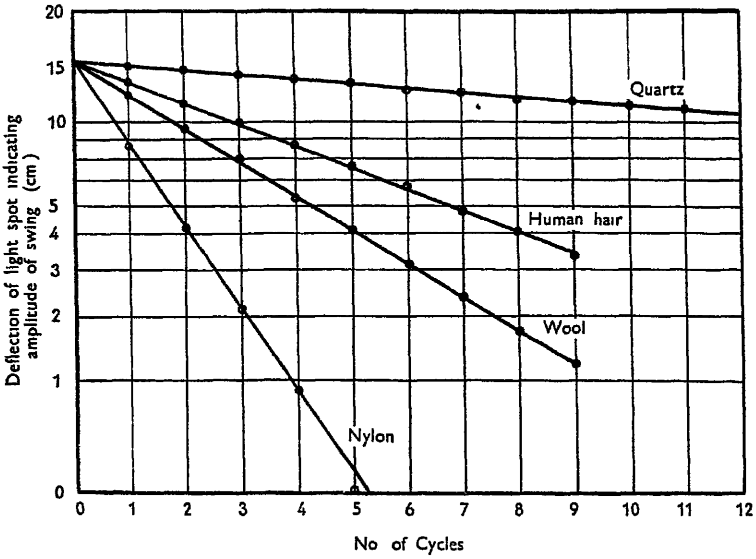

Fig. 2
Decay curve for damped torsional oscillations of a disc suspended from various fibres.

The decay curve is recorded by reading the deflection of a light spot reflected *via* the disc onto a scale The decay curve can also be recorded directly onto a moving photographic film, if required

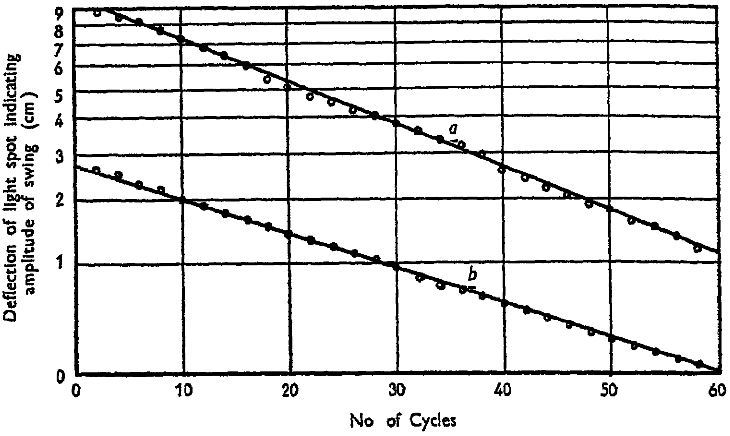

Fig 3
Decay curves for damped torsional oscillations of a disc suspended from a quartz fibre in air (*a*) and in a vacuum (*b*).

The modulus of rigidity N for the fibre of Fig 1 is measured by measuring the natural period of oscillation of the disc by means of a stop watch, and is given by[7]

$$N=\frac{128\pi I_m l}{T^2D^4} \quad . \quad . \quad . \qquad (4)$$

where I_m = moment of inertia of the disc about the diameter
l = length of fibre
T = period of oscillation
D = diameter of fibre

Using this formula, the moduli of rigidity of different fibres were determined and tabulated in Table II.

All these readings were taken in a vacuum, but could equally well have been taken in air.

MEASUREMENT OF YOUNG'S MODULUS FOR BENDING OF A FIBRE

The measurement of Young's modulus for bending of a fine fibre by static methods presents considerable difficulties On the other hand, it is a very simple matter when dynamic methods are employed

It can be shown[8] that for a free bar, clamped rigidly at one end, the fundamental frequency and overtones of transverse vibrations are given by

$$F=\frac{\pi(4S\pm1)^2}{8}\cdot\frac{K}{l^2}\sqrt{\frac{E}{\rho}} \quad \text{Cycles/sec. approximately}$$

where S is zero or an integer, K its radius of gyration about the neutral axis, l its length, E Young's modulus for the material and ρ its density In the case of the fundamental ($S=O$) the expression is approximate only and a more accurate value of F is obtained by substituting the value 1 19372 for the quantity $(4S+1)$

For the determination of Young's modulus we are interested only in the fundamental mode of vibration Substituting for $(4S+1)$ the value 1·19372, equation (1) reduces to

$$E=51\cdot1\,\frac{\rho F^2 l^4}{D^2}=51\cdot1\,\frac{\rho}{D^2}(l-{}^{1}/\sqrt{F})^4 \text{ dynes/cm}^2$$

for a circular bar

In our experimental determination of Young's modulus for bending of fine fibres a straight fibre, about 1 cm long, was selected and clamped at one end in sealing wax. The fibre was then viewed through a travelling microscope and excited to resonate at its fundamental frequency

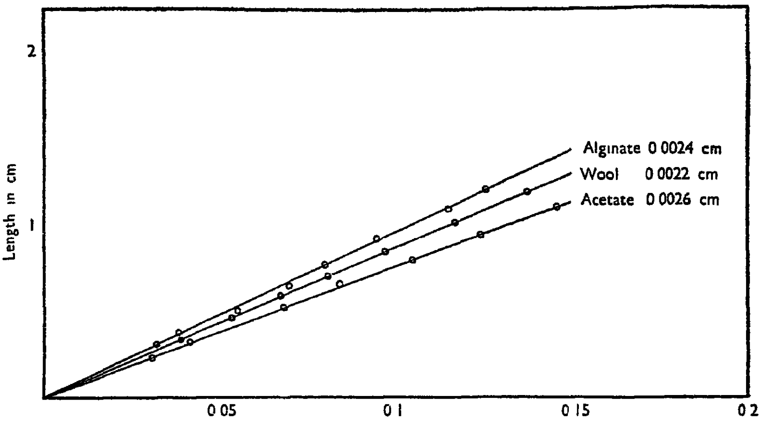

Fig 4
Curves of fibre length *vs* reciprocal of square root of fundamental transverse resonant frequency

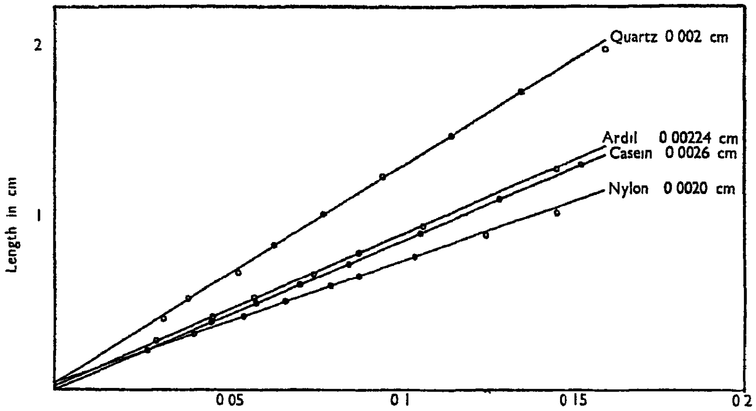

Fig 5
Curves of fibre length *vs* reciprocal of square root of fundamental transverse resonant frequency

The length of the fibre was reduced in steps and the resonance frequency for different lengths of fibre measured. A curve of length *vs.* $\frac{1}{\sqrt{F}}$ was plotted. Figures 4 and 5 give curves of length *vs.* $\frac{1}{\sqrt{F}}$ for different materials

These curves are all straight lines which should pass through the origin However, on account of imperfections in clamping, the effective length may be slightly greater when the fibre is loose or slightly less than the measured length when the sealing wax flows along the surface.

By plotting l *vs* $\frac{1}{\sqrt{F}}$ and taking the slope of the curve $\frac{dl}{d^1/\sqrt{F}}$ it is possible to obtain a more accurate value for E using the formula

$$E = 51\cdot 1\ \frac{\rho}{D^2}\left(\frac{dl}{d^1/\sqrt{F}}\right)^4 \qquad \text{dynes/cm}^2$$

Figs. 4 and 5 and Table I give results obtained with various fibres

The accuracy in calculating E depends on the accuracy to which ρ, l, D and F can be measured. The values of ρ for the different materials were obtained from tables, but could also be measured by submersion in liquids. The length l was measured with a travelling microscope to ±0·1 per cent. and the mean diameter D by means of a calibrated projection microscope to ±2 per cent. In this connection it should be noted that the square of the diameter enters into the calculation. Textile fibres show a greater or smaller degree of swelling with adsorption of water vapour, and the diameter should consequently be determined under the same conditions of temperature and humidity as the frequency of vibration, or the necessary corrections should be applied. The accuracy of the frequency as indicated on the dial of the calibrated resistance coupled oscillator used for excitation of the fibre was ±1 per cent

EXCITATION OF THE FIBRE

The fibre can be excited in two ways:

(*a*) The fibre can be placed in the sound field of a loud-speaker driving unit, as shown in Fig. 6b, and the frequency adjusted until resonance of the fibre is observed; or

(*b*) the fibre can be excited, by means of a disc recorder cutting head as shown in Fig. 6c, or a magnetic driver as shown in Fig. 7a. There will be a slight difference in resonant frequency, depending on the method of excitation, due to a difference in air loading in the two cases.

Fig. 8 gives three resonance curves for a quartz fibre 0·62 cm. long and 0·003 cm. diameter, taken under different conditions.

Curve (*a*) was taken in a vacuum with an electromagnet as exciting unit (Fig. 7b).

Curve (*b*) was taken in air by means of the same apparatus

Curve (*c*) was taken in air and with sound field excitation.

From these curves it will be seen that the resonance curve is very much sharper when taken in a vacuum (as indicated by the values of Q) than when taken in air. This is due to air friction Furthermore, there is a reduction in resonant frequency when taken in air due to the mass of a layer of air moving bodily with the fibre and due to the frictional resistance of the air. It is found, however, that when the fibre is excited by a sound field the resonance frequency is very close to that in a vacuum and the resonance curve is also sharper than when the fibre is excited by the electromagnet in air. On the other hand, even if the fibre is excited by the electromagnet, the

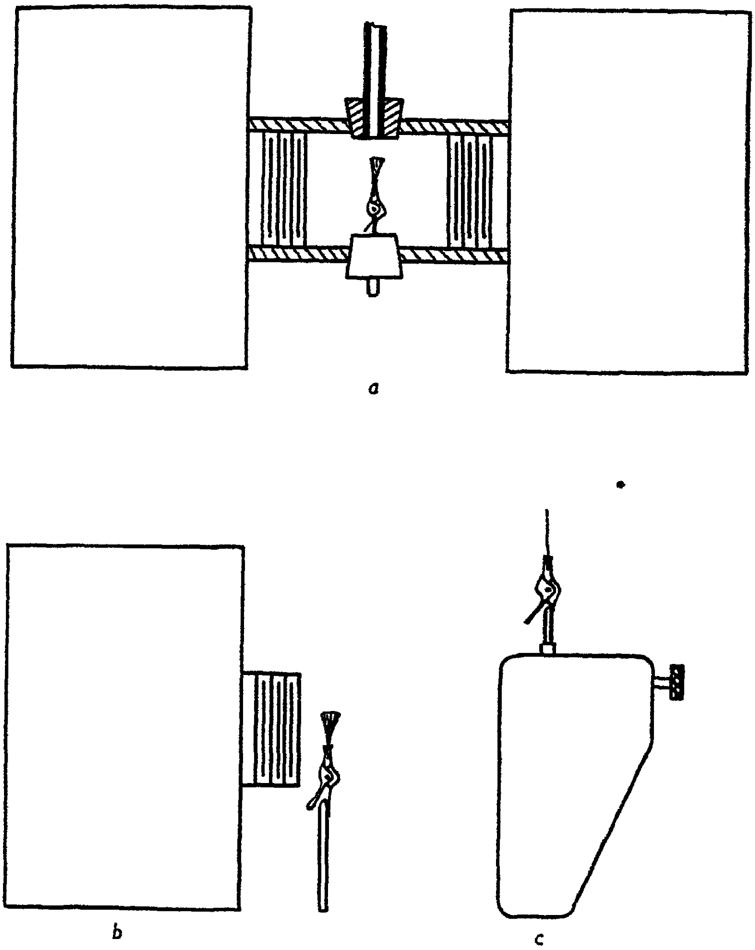

Fig 6

(*a*) Loudspeaker driving units for measuring Young's modulus of a fibre in an enclosed space

(*b*) Loudspeaker driven unit for measuring Young's modulus of a fibre under atmospheric conditions

(*c*) Disc recorder cutting head used as a driving unit

error in resonant frequency due to the surrounding air is still well within the experimental error of frequency measurement if we measure frequencies to ±1 per cent.

Therefore, either a sound field or an electromagnet may be used for driving the fibre If an electromagnet is used, then care must be taken not to work too close to any of the resonance frequencies of the mechanical system A stroboscope can be used to determine whether the vibration observed is a resonance of the fibre or a vibration of the mechanical system

If it is required to determine the effect of humidity on fibres, then either the apparatus of Fig. 6a, consisting of two loud-speaker units connected by a transparent tube or the apparatus of Fig. 7b can be used The latter is the less reliable method.

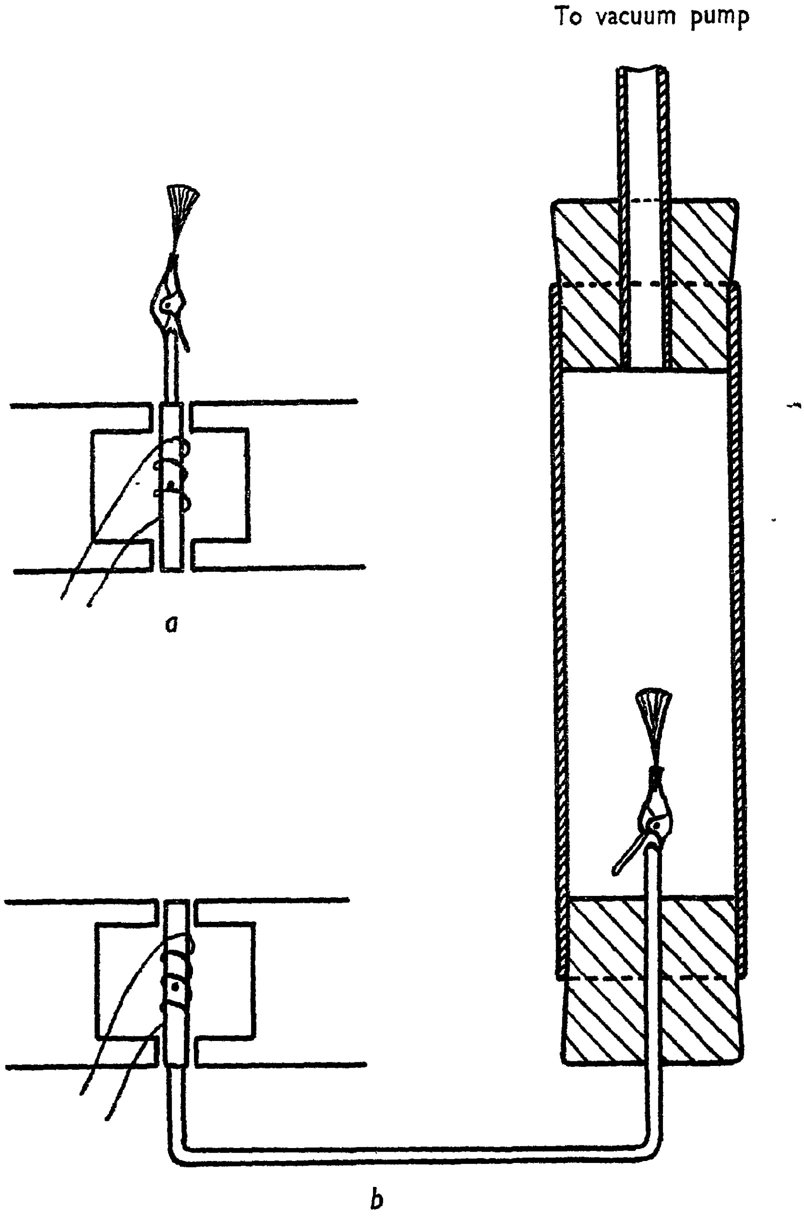

Fig. 7

(*a*) Electromagnetic exciter unit used for measurement of Young's modulus for bending of fibres

(*b*) Fibre excited under controlled conditions by the same unit

Curvature of the fibre should be avoided if possible, by selecting straight portions Should a slight curvature be unavoidable, the fibre should be made to vibrate in the plane of curvature in order to reduce possible torsion to a minimum

APPROXIMATE METHOD FOR THE DETERMINATION OF DAMPING CAPACITY FOR BENDING OF A FIBRE

An attempt was made to determine the damping capacity from the resonance curve of the fundamental transverse vibration of a fibre clamped rigidly at one end

The theory of transverse vibrations of a rod with internal and external losses, even when simplified as far as possible by the omission of quantities of secondary importance, is still very complex and it was found to be practically impossible to determine the exact relation between damping capacity and the sharpness of resonance of the fundamental mode of transverse vibrations. Furthermore, the sharpness of resonance depends to a large extent on the method of excitation of the rod

An approximate relation between damping capacity and sharpness of resonance is obtained by considering the fibre vibrating in its fundamental mode as a system of one degree of freedom. The sharpness of resonance of such a system is usually expressed by the symbol

$$Q = 2\pi F m / r \qquad (5)$$

where m is the lumped mass, r the mechanical resistance and F the resonant frequency

The Q of the system at resonance is, therefore, defined as the ratio of the total reactance of the mass to the total resistance of the system, including that of the generator If ΔF is the difference in frequency between two points on the resonance curve, where the amplitude is 70 7 per cent of its maximum value, then

$$Q = \frac{F}{\Delta F} \qquad (6)$$

If the resonance curve is recorded, then the Q can be determined graphically and the logarithmic decrement determined from the formula

$$\delta = \frac{\pi}{Q} = \frac{\pi \Delta F}{F} \qquad (7)$$

as in the case of the torsional resonant system the damping capacity is given by equation (3), *viz* ,

$$\psi = 1 - e^{-2\delta}$$

Resonance curves for short fibres of different materials were obtained in a vacuum (see Fig 7b) by observing the fibre through a travelling microscope and measuring the amplitude of vibration by means of its graduated scale over the resonance frequency region, while excited by a resistance coupled oscillator and electromagnet The exciting current was kept constant over the whole region Q was determined for the resonance curves and δ and ψ calculated The results are tabulated in Table II

The fibres for which the damping capacities were measured by this method were the same as those used when the damping capacities were measured under torsion in a vacuum, the results of which are also tabulated in Table II

It will be seen that there is a close agreement between the damping capacities as measured by the two methods In the case of wool the damping capacity for bending is higher than for torsion for the two samples tested and the ratio of damping capacity for bending to damping capacity for torsion is approximately equal in the two cases In the case of cellulose acetate the value for bending is also higher than the value for torsion

The value of ψ is independent of length of fibre when measured in torsion, but when measured for bending by this method there is a certain variation with length.

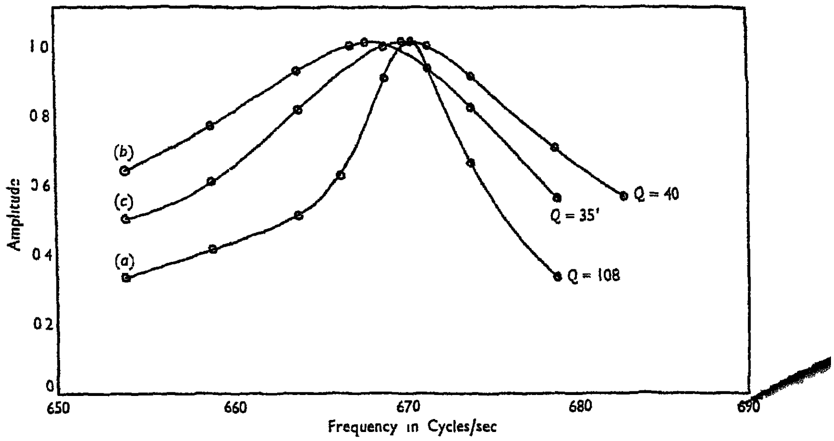

Fig. 8
Resonance curves for a quartz fibre 0·62 cm. long, 0·0030 cm diameter excited by an electromagnet in vacuum (*a*), by an electromagnet in air (*b*), and by a sound field (*c*).

The disadvantage of the vibration method is that the experiment can be carried out only in a vacuum in order to avoid air friction losses which are of the same order of magnitude as the internal losses It may, however, be possible to take measurements under atmospheric conditions and make a correction for air friction.

Table I
Young's modulus (*E*) for bending of textile fibres measured by transverse vibration under atmospheric conditions. No account was taken of temperature, humidity, etc , and the values obtained are merely to illustrate the method and are by no means average values

Material	Diameter (cm)	$\frac{dl}{d^1/\sqrt{F}}$	ρ (gms /c c.)	*E* (dynes/cm ²)
				×10¹¹
Ardil .	0·00224	8·7	1·3	0·760
Quartz	0·0020	12·4	2·65	8·01
Casein . . .	0·0026	8·6	1·30	0·538
Nylon . . .	0·0020	7·0	1·146	0·352
Alginate . .	0·0024	9·4	1·78	1·230
Wool .	0·0022	8·6	1·31	0·747
Acetate . .	0·0026	7·4	1·30	0·295

Table II
Damping capacity for torsion and bending of textile fibres taken in a vacuum. The values tabulated are not average values

Material	Diameter in cms	Torsion in vacuum				Bending in vacuum		
		Length	*N*	δ	ψ	Length	δ	ψ
		cm.	Dynes/cm ² ×10¹¹			cm		
Quartz	0·00321	7·91	1·315	0·025	0·030	0·91	0·028	0·035
Human hair .	0·00721	7·48	0·05715	0·130	0·231	1·16	0·129	0·228
Wool . .	0·00254	6·00	0·4753	0·207	0·329	0·73	0·326	0·479
Wool	0·00354	5·91	0·153	0·140	0·258	0·59	0·209	0·342
Nylon	0·00204	6·89	0·2606	0·458	0·600	0·77	0·491	0·625
Acetate	0·00260	5·466	0·05793	0·250	0·393	0·668	0·403	0·552

ACKNOWLEDGEMENTS

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REFERENCES

Speakman *J Soc Chem Ind*, 1930, **49**, T209

[2] Carlene *J Text Inst*, 1947, **38**, T38

[3] Yousef *Phil Mag*, 1946, **37**, 490.

[4] Foppl *J Iron and Steel Inst*, 1936, **11**, 393

[5] Thomson and Traill *J Text Inst*, 1947, **39**, T43

[6] Speakman. *Trans Farad Soc*, 1929, **25**, 92

[7] Morley *Strength of Materials*, page 410

[8] A B Wood. *A Text-book of Sound*, page 117

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14—MOISTURE ABSORPTION, DENSITY AND SWELLING PROPERTIES OF NYLON FILAMENTS*

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INTRODUCTION

Previous work has shown that nylon yarn as it comes from the spinning mill is in a quasi-stable state, and that certain treatments such as steaming or immersion in water will relax it, as evidenced primarily by a decrease in length This is apparent in the preboarding operation for nylon hose, and in the finishing of nylon fabric, as well as in certain other commercial operations There is, in fact, some demand in the textile trade for nylon yarn which has been preshrunk so that no further dimensional change will take place during subsequent processing

The practical and scientific interest associated with this length contraction as well as with other features of nylon behaviour suggested a value to be gained from investigating some of the physical properties of nylon in greater detail. In the present paper experimental data showing the dependence of moisture content, density and dimensions on relative humidity are recorded for both drawn and undrawn nylon filaments These properties are closely interrelated, and a knowledge of them is basic to further studies which it was desired to undertake on the effect of steam treatment on nylon fabrics It was anticipated that features of interest in connection with fibre structure and nylon filament behaviour might be exhibited by comparison as well as individual examination of results on nylon in both the drawn and undrawn states. For this reason undrawn as well as drawn filaments were included in the investigations and the results obtained fully justified this approach to the work

In a comprehensive paper on the physical properties of nylon, Speakman and Saville[1] have recorded their experimental findings on the regain-relative humidity relationships of drawn and undrawn nylon, together with data on longitudinal swelling and density for drawn nylon filaments Certain of the findings of these investigators, however, showed differences from similar observations made in our laboratory. Since it did not appear reasonable to attribute these differences simply to the source of nylon used, investigation of possible reasons for the apparent discrepancies was indicated, and certain extensions to the work were pursued as a result

In all the work to be reported type 66, 3 denier per filament, semi-dull, normal tenacity, unsized, unoiled yarn was used for the drawn nylon, and the undrawn sample consisted of the corresponding material before drawing

A. MOISTURE ABSORPTION BY NYLON

1. The Effect of some Liquid Treatments on Moisture Absorption

If nylon yarn received from the spinning plant is dried over a suitable drying agent without any pretreatment and then taken through a series of humidities up to saturation and back to dryness, a marked hysteresis in the moisture regain is to be found The absorption curve so obtained is, however, no longer reproducible and further cycles of humidity give regain values which agree closely with those read from the original desorption curve, whether the humidity at which the measurement is made is approached from the higher or lower side. Wetting in water would therefore appear to bring about an irreversible change in the moisture absorption properties; and it is conceivable that treatment with other liquids might similarly effect some modification in the amount of absorption. To investigate this possibility and to verify the irreversible change occasioned by immersion in water, experiments were conducted in which both drawn and undrawn nylon were subjected to several treatments and the regains determined at a selected relative humidity.

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* This paper was presented in part at the 1948 Annual Conference of the Chemical Institute of Canada

Experimental

The moisture content at any relative humidity was determined by weighing a bundle of filaments which had been dried to constant weight over anhydrous magnesium perchlorate and subsequently conditioned over a suitable concentration of sulphuric acid solution.[2] The same sample was used for all humidities, and approximated 1 gram in weight.

The nylon bundle was suspended by means of a gold wire inside a weighing bottle containing the sulphuric acid solution. The wire, which extended through a short glass tube in the stopper of the bottle, could be hooked directly to the arm of an analytical balance for weighing. While the filaments were conditioning, the end of this glass tube was covered with a glass cap seated in rubber. Under these conditions, the filament bundle was supported on a small perforated platform from which it could be raised clear when attached to the balance arm. The weighing bottle was stored, well lagged, inside a capped glass jar which was then suspended in a water-bath operating at 70° ± 0·1° F. The jar was removed from this water-bath only for weighings to be made, and the brief interval of time required for this purpose, having regard to the heavy lagging, was not sufficient for the conditions inside the weighing bottle to change sensibly. Weighings were made on successive days until checks were obtained to within ±0·0002 g. Assuming equilibrium, this provides regain values reliable to ±0·04. In the figures to be quoted, values of regain are recorded to the nearest 0·05.

Table I

Treatment	Regain	
	Drawn nylon	Undrawn nylon
Dried, and exposed to 89% R.H.	6·45	7·90
Immersed in water at room temperature for 24 hours. Dried and exposed to 89% R.H.	6·70	8·00
Re-dried and exposed to 89% R.H.	6·75	7·90
Immersed in ethyl alcohol at room temperature for 4 hours. Washed in water, dried and exposed to 89% R.H.	7·25	8·40
Immersed in saturated aqueous solution of benzoic acid at room temperature for 18 hours. Washed in water, dried and exposed to 89% R.H.	7·00	7·90
Immersed in 1% aqueous *m*-cresol at room temperature for 18 hours. Washed in water, dried and exposed to 89% R.H.	6·20	7·10

In a first series of experiments, samples of drawn and undrawn nylon were taken directly off the spool shipped from the plant and after suitable bundles had been prepared, these were taken through a series of treatments which included soaking in water, ethyl alcohol, and aqueous solutions of benzoic acid and *m*-cresol, in that order. The latter two reagents were chosen primarily because of their more pronounced influence on swelling. Thorough washing in water followed the treatment with alcohol, benzoic acid or *m*-cresol solution and included soaking in water for a minimum of 24 hours. The regain values were determined at 89 per cent relative humidity. In Table I are shown the results of these experiments together with more detail of the actual treatments to which samples were subjected.

The salient features of these results will be discussed in more detail later, but it should be noted in passing that the ability of drawn nylon to absorb moisture at high humidities is increased by immersion in water, while undrawn nylon is not appreciably influenced in this way. Moisture absorption by both drawn and undrawn nylon is increased by immersion in alcohol, but decreased again by treatment in saturated benzoic acid solution. A still further marked decrease is occasioned by immersion in dilute *m*-cresol.

In a second series of experiments, the nylon samples were soaked in water prior to the first weighing and regain values were then determined under absorption and desorption conditions at 59 per cent. and 90 per cent. R.H. The effect of ethyl alcohol treatment on the regain was then also investigated at 59 per cent R H. approached from both the dry and wet sides. The results are shown in Table II.

Table II

Treatment	Regain	
	Drawn nylon	Undrawn nylon
Dried, and exposed to 59% R H (absorption)	4·05	4·15
Soaked in water at room temperature for 24 hours, exposed to 59% R H. (desorption)	4·05	4·15
Dried and re-exposed to 59% R.H. (absorption)	4·00	4·10
Exposed to 90% R H. (absorption)	6·90	8·00
Saturated and re-exposed to 90% R.H. (desorption)	7·00	8·10
Dried, immersed in ethyl alcohol at room temperature for 18 hours, washed in water, dried and exposed to 59% R H (absorption)	4·10	4·20
Saturated and re-exposed to 59% R H (desorption)	4·20	4·25

These experiments show that hysteresis in nylon is very small or non-existent, and that treatment with alcohol has a much less pronounced effect on the moisture absorption at 59 per cent. relative humidity than it has at 89 per cent. relative humidity (see also Table I)

2. The Regain-Humidity Relationships of Drawn and Undrawn Nylon

Because a nylon fabric invariably receives wet finishing treatment in the course of manufacture, knowledge of the complete regain-relative humidity relationship for nylon which has previously been soaked in water is important In addition, there are obvious advantages in using nylon so treated in further studies of the filament because of the greater stability induced by pre-wetting. Experiments to determine the regain values from dryness to saturation for both drawn and undrawn nylon, previously wetted, were therefore conducted. The fact that treatment with ethyl alcohol had been shown to modify the moisture absorption properties of nylon, and that this reagent was used by Speakman and Saville as a solvent for purification prior to their measurements of regain, suggested that a sample of drawn nylon which had been subjected to immersion in alcohol should also be included

Experimental

Skeins of drawn and undrawn nylon weighing about 10 grams were reeled and immersed in water at room temperature for 48 hours, followed by drying over anhydrous magnesium perchlorate for a similar period. The wetting and drying were then repeated a second time to ensure that water at room temperature would not be likely to effect any further change. One skein of drawn nylon was then immersed in ethyl alcohol at room temperature for 5 hours, thoroughly washed with several changes of water, left immersed in water for 18 hours, rewashed and left in fresh water for a further 24 hours and finally dried.

For relative humidities from 23 per cent. to 66 per cent., the prepared skeins were exposed in a closely controlled conditioned room operating at a temperature of 70° F (21·1° C.), and weighings were taken to the nearest milligram. The initial dry weights were obtained by introducing the skeins into Nesbitt type absorption bottles through which dry air could be passed until constant weights had been reached. For the higher and lower humidities, bundles weighing approximately 1 gram were cut from each skein and a technique similar to that previously described was adopted. Because nylon which has been pre-treated with water or alcohol shows little or no hysteresis, regain values taken under absorption conditions only were investigated.

Results

The results of the regain experiments are given in Table III, and columns 2 and 3 are shown graphically in Fig. 1.

Table III

Relative Humidity %	Regain		
	Drawn nylon (water treated)	Undrawn nylon (water treated)	Drawn nylon (alcohol treated)
8·5	0·70	0·65	0·75
23	1·65	1·50	1·70
29	1·95	1·85	2·00
35	2·40	2·30	2·50
47	3·30	3·20	3·35
66	4·50	4·75	4·75
79·7	5·75	6·35	—
89·9	6·85	8·00	7·25
98·2	8·1	10·0	—
99·3	8·6	10·6	—

The sample treated with alcohol has been omitted from the graph to avoid confusion, but its curve will be seen to follow closely the drawn nylon sample in the lower humidity range and finally to occupy an intermediate position between the drawn and undrawn samples at high humidities. It will also be observed that appreciable divergence of the curves for drawn and undrawn nylon occurs only in the upper half of the relative humidity range.

3. Discussion

The results of the preceding experiments exhibit several features of interest, particularly in relation to considerations of fibre structure. X-ray diffraction photographs show a high degree of orientation for drawn nylon, and a lack of orientation but definite crystallinity for undrawn nylon. P. H. Hermans and others have given evidence that water is absorbed only in the amorphous regions; and there is reason to believe that filaments possessing a highly oriented structure will tend to absorb less water than otherwise similar filaments showing a smaller degree of orientation.

A decrease of water absorption cannot, however, be explained simply in terms of orientation, for it has been shown that the amount of water absorbed by undrawn nylon can be increased. A decrease in the capacity of a fibre to absorb moisture could be caused either by an increase in the volume of

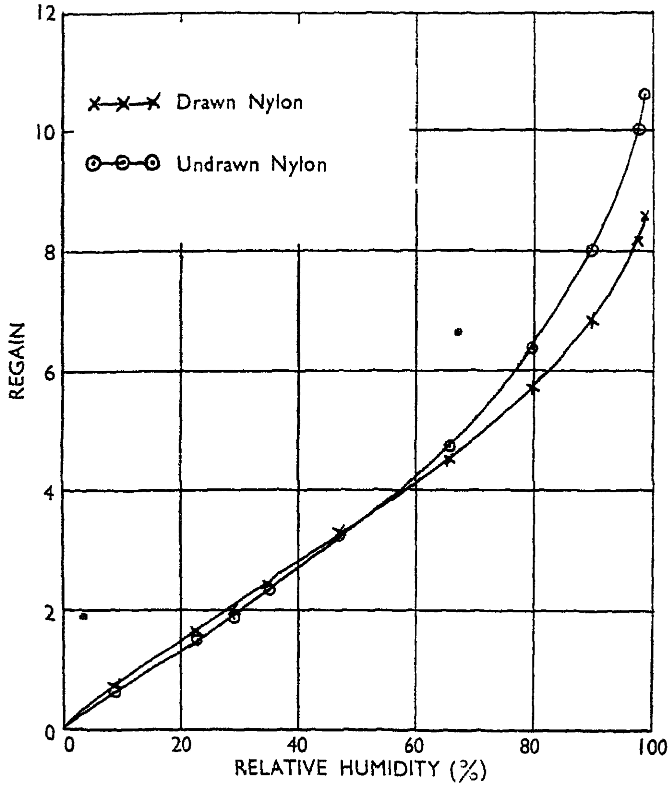

Fig 1

the crystalline region, or by a decrease in the extent to which moisture can penetrate the amorphous region. Either or both of these effects could take place, of course, without necessarily affecting the degree of orientation as shown by X-ray diffraction. However, it seems reasonable to suppose that mechanical manipulation such as drawing which gives rise to increased orientation of the crystallites may, in effect, result in an increase in the proportion of crystalline substance through an aligning of neighbouring molecular chains in parts of the amorphous material, so that water molecules can no longer penetrate these particular regions On the other hand there is no reason to suppose that amorphous regions are completely or equally accessible throughout to penetration by water; and indeed there is growing evidence to show that this is not the case This point of inaccessibility within an amorphous region and the concept of varying absorptive capacity depending upon the precise pattern in the lie of molecular chains will be referred to again.

It is not unreasonable, therefore, to expect that an undrawn nylon sample would show higher values of regain than corresponding drawn material This has clearly been shown to be the case in the high humidity range It is not immediately evident, however, why a departure in behaviour between the two should not manifest itself more positively than has been found to occur in our results at relative humidities below 50 per cent., even though the absolute differences in regain in this region would not be anticipated to be great. From the experimental values given by Speakman and Saville it may also be observed that there is no divergence of the regain curves which is significantly greater than the experimental accuracy for comparable drawn and undrawn nylon samples between 15 per cent. and 45 per cent. relative humidity, although the curve of the latter lies slightly above that of the former The regain curve obtained in the present work for the sample of drawn nylon treated with alcohol similarly does not diverge significantly from the corresponding untreated sample until about the same level of humidity has been reached

The results obtained for the regain of nylon which had been pre-treated with ethyl alcohol correspond very closely with the published work of Speakman and Saville throughout the majority of the humidity range. Only at very high humidities do our results show lower values than those obtained by those authors This latter may probably be due to a difference in the conditions of the treatment with the ethyl alcohol which the yarn received Precise results correlated with the exact conditions of the alcohol treatment are not of any practical importance, however, since nylon is not normally treated with this reagent

The values of regain obtained at the same relative humidity under absorption and desorption conditions on both drawn and undrawn nylon (Table II) indicate the possibility of a slight hysteresis, but if present at all it must be very small. Speakman and Saville have previously reported no evidence of its presence, and White and Eyring[3] have recently pointed out on the basis of their thermodynamical treatment of water absorption that nylon would be expected to exhibit little or no hysteresis.

The effect on the moisture absorption properties occasioned by treating nylon with different reagents is interesting. it is readily possible to bring about an increase or decrease in the absorption from its normal level. The liquids water, ethyl alcohol, saturated aqueous benzoic acid solution, and a 1 per cent aqueous solution of *m*-cresol were chosen because of their reported effect on swelling in the order given. The results obtained cannot be related simply to the swelling powers of these reagents, however, since ethyl alcohol raises the regain the most and *m*-cresol solution reduces it to a point considerably below that of the untreated filament. In some work recently published by Bergmann, Fankuchen and Mark[4] it is shown that soaking in an aqueous solution of phenol increases the degree of orientation of a drawn nylon filament A decrease in moisture absorptive capacity might therefore be anticipated to result from this treatment The effect of a lowered regain from treatment with *m*-cresol might similarly be explained as an increase in the degree of orientation or crystallinity, but it would have been expected to have a more pronounced effect on undrawn than drawn nylon whereas the regain change is approximately the same in both cases Again, in this latter connection, although soaking in water has a more marked influence on drawn nylon than undrawn in raising the regain, the increase brought about by treatment with alcohol is of similar magnitude for both No explanation of these changes sufficiently conclusive can be offered on the basis of evidence presented here, but the fact that they can be brought about warrants further consideration because of both a theoretical and practical interest associated with them

B. THE DENSITY OF NYLON

4. General

A value of density necessarily involves the meaning to be attached to volume. In the case of textile fibres, if volume is measured by displacement when immersed in a liquid or gaseous medium the result will depend upon whether there is penetration by the fluid and the degree to which this can occur. The volume measured in a non-penetrating medium such as benzene, for example, is higher than that measured in a liquid capable of penetrating the fibre such as water. The density figures are therefore correspondingly lower in benzene than in water except at saturation regain. It is generally accepted that what is referred to as a true density has as its basis the macroscopic fibre volume; and that figures obtained from measurements in penetrating fluids are therefore apparent densities. This understanding will be followed in connection with the results here to be discussed.

Absorption of moisture into a dry textile fibre is accompanied by a change in volume, and the density at any given moisture content is an unpredictable value describing this new mass-volume relationship. The relationship of apparent density in water to moisture content on the other hand is calculable for the whole range of regain provided any one value is known, because it is a ratio of a mass to that volume which is displaced when the fibre is immersed in water, the latter quantity therefore being uninfluenced by regain. The figures obtained from density measurements in a non-penetrating liquid and those for the apparent density in water are important and useful. True densities have been measured in the present work on drawn and undrawn nylon for a range of moisture contents between dry and saturated conditions. The apparent density in water of drawn and undrawn nylon has also been determined.

5. True Density

Experimental

The chief difficulty encountered in all measurements of density of textile fibres is the elimination of entrapped or adhering air. Its inclusion necessarily results in values which are too low. Picnometric methods have been extensively employed, but the difficulties attendant upon obtaining an accuracy to three decimal places have in our experience been found to be so great that alternative methods were given consideration. This degree of accuracy is particularly important in the case of nylon where the need is emphasised by the fact that the maximum variation in density with moisture content is less than one per cent.

P. H. Hermans[5] has described a flotation method which appears to minimise the errors of picnometric estimation In this technique small pellets of short fibre are immersed in a suitable liquid and the density of the liquid medium varied either by addition of a second liquid of different density or by change in temperature until flotation is achieved. The danger of disturbances due to convection currents in the liquid and the somewhat tedious care necessary to obtain the accuracy desired suggested trying a modification involving centrifuging. In this procedure a small amount of filament cut to about 1 mm in length was placed in a small culture tube and conditioned in an atmosphere of known relative humidity inside a suitably capped container placed in a thermostat. When sufficient time had elapsed to assure equilibrium having been reached, the container cap was removed and the filaments rapidly covered with a few c c of a liquid judged to be of a suitable density. The contents of the culture tube were then carefully transferred to a 15 c.c. centrifuge tube and filled with the same liquid At this time the filaments formed a uniform cloud throughout the tube. The tube was then centrifuged for 2 minutes at 3400 r.p.m. which gives a centrifugal acceleration of about 2400 g at the tip of the tube It was found that the deceleration of the centrifuge produced sufficient currents in the liquid to disturb the settling of the filaments somewhat when the liquid had a density very close to that of the filament. An accumulation of fibre rather than uniform dispersion was considered evidence that the liquid and fibre densities were not the same, and subsequent behaviour in the space of one or two minutes after removal from the centrifuge usually confirmed this by the accumulation of fibre showing a tendency to sink or float.

Measurements were made on drawn filament, undrawn filament, and 1100 denier monofilament The latter approximated drawn filament in so far as it was highly oriented, and it was found particularly definite in its behaviour toward centrifuging. All samples were cut from filaments previously taken through two cycles of soaking in water for 24 hours and drying over anhydrous magnesium perchlorate, and the subsequent conditioning was carried out at a temperature of 70° F The liquids employed were made up from mixtures of nitrobenzene and benzene covering a density range of 1·140 to 1·151 in a series of seven steps The densities of these liquids were measured picnometrically.

Results

The temperature change during the course of the series of experiments was not more than 1° C. Centrifuging effected a small temperature rise but the results can be said to be represented by a mean temperature of 21·5° C. The temperature coefficient of the liquid mixture employed is 0·001 g./c.c /° C., and without affecting the accuracy of the results appreciably the density figures may be taken as representing values at 70° F.

It was possible to detect a difference in behaviour of similarly conditioned samples of fibre in two liquids having a density difference of 0·002 to 0·003 g. per c.c. The results obtained are therefore considered accurate to ±0·001 g. per c.c. The well-defined behaviour of the heavy monofilament provided results considered more reliable than those for the finer drawn and undrawn filaments, but it will be seen that the values obtained for the drawn filaments and the monofilament cannot be differentiated and so are plotted together as one curve Since it is apparent that orientation does not produce any very great difference in density, and both the drawn and monofilament samples show good orientation this close similarity in density is not surprising

The results obtained are given in Table IV.

Table IV

Relative Humidity %	Density (g per c.c)		
	Undrawn	Drawn	Monofilament
0	1·141	1·146	1·144
20·0	1·142	1·146	1·147
50·0	1·144	1·149	1·149
65·7	1·147	1·150	1·150
90·0	1·144	1·149	1·150
98·0	1·144	1·150	1·149

6. Apparent Density in Water

The apparent density in water was measured for both drawn and undrawn nylon, and the method used was one described by P. H. Hermans Bundles of fibre weighing about one gram were pretreated by soaking in water at room temperature for 24 hours, drying over anhydrous magnesium perchlorate for 24 hours, soaking in water again for 24 hours and then re-drying over magnesium perchlorate to constant weight Each bundle was then immersed in distilled water which was boiled for 10 minutes under reduced pressure at about 45° to 50° C to eliminate entrapped air. After soaking for 18 hours in the water in which it was boiled, the bundle was weighed while still immersed. Calculation of the apparent densities gave the following values.

Drawn nylon	1·166 g per c c
Undrawn nylon . .	1·164 g. per c c

Due to the difficulty of ensuring complete elimination of all air, these figures are probably not reliable to more than *±0·002 g* per c c. However, the consistently lower values obtained for undrawn nylon in replicate experiments leave little doubt that its apparent density is slightly less than that for drawn nylon.

It might at first be expected that undrawn nylon with its lack of orientation would give rise to more ready and complete penetration of the amorphous region by water than drawn material, with consequent higher apparent density. It is to be remembered, however, that a lower true dry density is an offset to a lowered volume measured in water. The penetration of undrawn nylon is evidently not sufficiently greater than that of drawn material to offset the difference in their true densities. This conclusion is borne out by a calculation of the amount of space in the filament which is accessible to water.

The volume of space inside the filament penetrated by water is the difference between the volume measured in benzene and that measured in water. The volumes calculated from the experimentally determined values for the true density and apparent density in water of dry nylon are shown below.

	Drawn nylon	Undrawn nylon
Volume of benzene displaced by 1 g dry nylon .	$\frac{1}{1\cdot145} = 0\cdot874$ c c	$\frac{1}{1\cdot141} = 0\cdot876$ c c
Volume of water displaced by 1 g. dry nylon . .	$\frac{1}{1\cdot166} = 0\cdot858$ c c	$\frac{1}{1\cdot164} = 0\cdot859$ c c
Volume of space penetrated by water	0·016 c c	0·017 c c

In the case of drawn nylon the calculation shows the space penetrated by water to be 0·016 c c per g of dry filament or 1·8 per cent of its dry volume. For undrawn nylon the corresponding value is 1·9 per cent of the volume of the dry filament, and the difference between drawn and undrawn nylon in degree of penetration is therefore small.

C. SWELLING PROPERTIES

7. Effect of Immersion in Water on Filament Length

The first evidence that a permanent contraction accompanies moisture absorption in filaments as received direct from the spinning mill was indicated to us in carrying out some early experiments on longitudinal swelling. In taking a filament through a series of ascending humidities it was found that when the higher humidities were reached, an apparently anomalous behaviour was exhibited in the amount of swelling. Re-drying the filament showed that the dry length was now less than that originally measured. When the filament was again exposed to a high humidity further contraction occurred and only after it had been thoroughly wetted out in water could reproducible results of longitudinal swelling be obtained throughout the whole of the relative humidity range. It was decided to investigate in more detail the effect on length of drawn and undrawn nylon filaments occasioned by soaking in water at room temperature, and of repeated cycles of wetting and drying.

Apparatus was set up whereby a 75 cm length of filament was mounted in a glass tube through which dry air could be passed, or which could be filled with water. The drawn filaments were made to carry at their lower ends four 75 mg. lead weights which normally rested on a small platform, but which, when supported by the filament, did not cause any permanent extension. By measuring the filament lengths successively under one, two, three and four weights an extrapolation could be made to obtain an estimate of the length under zero load. It was not possible to set up the undrawn filaments in a similar way since the addition of anything more than a very small weight tends to stretch them permanently. A single weight was therefore used, which was just heavy enough to keep the filament straight but not enough to cause stretching (*ca.* 15 mg.).

Each filament was first dried in moisture-free air and its length measured to the nearest 0·25 mm. It was then immersed in water at room temperature for not less than 24 hours, again dried and its length re-measured. This cycle was repeated several times, but it was found that a sensibly reproducible value occurred after the first wetting.

The amount of contraction resulting from wetting was not uniform from filament to filament as is illustrated by the following results:

Drawn filament: 3·4, 2·0, 3·3, 3·1, 2·5, 2·6% Average: 2·8%
Undrawn filament: 1·0, 0·9, 1·8, 2·0, 0·6, 0·8% Average: 1·2%

After the first cycle of wetting and drying the dry length was reproducible to within ±0·1 per cent. It was clear that before accurate swelling measurements could be made, this initial contraction on wetting had to be allowed to take place. All filaments for further study were therefore subjected to two preliminary cycles of wetting and drying, allowing 48 hours in water at room temperature each time.

8. The Longitudinal Swelling of Nylon

Drawn and undrawn filaments which had previously been allowed to contract by immersing in water were taken through relative humidities ranging from dryness to saturation (water immersion). Lengths of about 85 centimetres were used, and measurements were made to the nearest 0·01 cm. at each humidity step. A method of extrapolation previously described was employed for the drawn filaments to obtain the length under zero load. Temperature was maintained at 70° F.

The averaged results from several filaments are given in Table V, and are shown plotted against regain in Fig. 2.

Table V

Relative Humidity %	Longitudinal Swelling %	
	Drawn nylon	Undrawn nylon
8·5	0·15	0·15
23	0·45	0·40
29	0·60	0·60
35	0·70	0·90
47	1·05	1·55
64	1·30	2·50
80	1·75	3·80
90	2·05	—
100	2·7	6·9

It will be seen from Fig. 2 that except for the early stages of moisture absorption, the longitudinal swelling bears a relationship to regain best represented by a straight line for all values which can be plotted, that is excluding the value at saturation. This relationship has also been shown to be true in the case of silk[6] up to and including the swelling in water In the present case the saturation values of longitudinal swelling on drawn and undrawn nylon were determined by immersion of the filaments in water, but the regains corresponding to saturation conditions are not known In Fig 2 the saturation swelling values have been inserted on straight line extrapolations of the swelling-regain relationships as representing not improbable behaviour. This treatment indicates the saturation regains for drawn and undrawn nylon to be 8 7 and 11 0, respectively

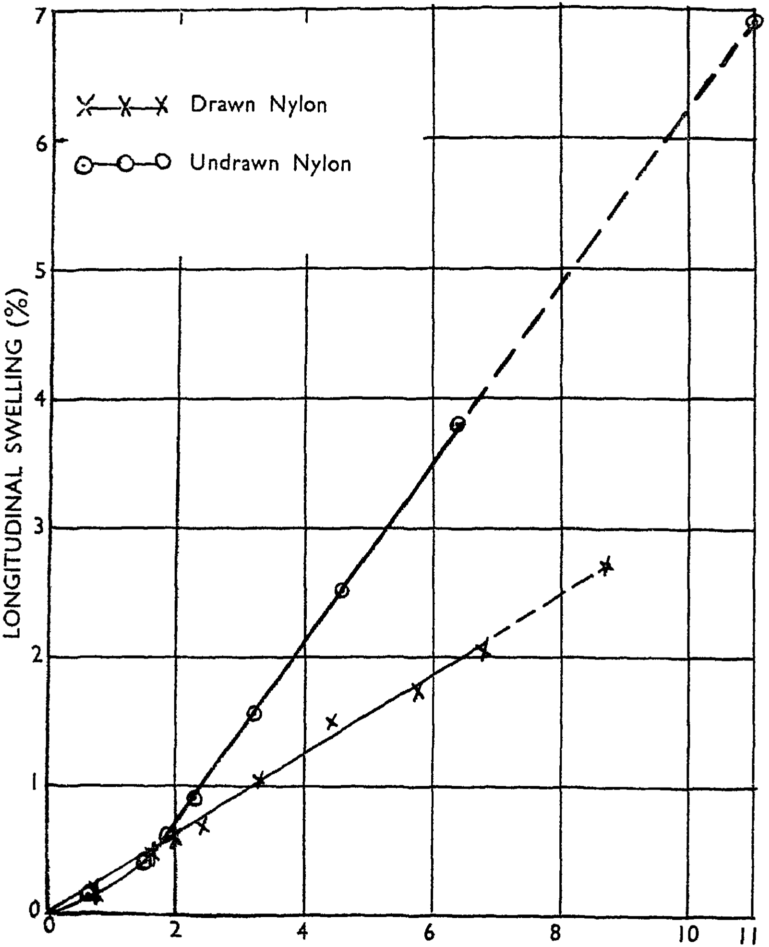

Fig. 2

The values obtained by Speakman and Saville for longitudinal swelling of drawn nylon filaments conform closely to the above values in the lower range of humidities but deviate widely at high humidities. The maximum swelling observed by these authors was 1 17 per cent with marked flattening of the curve beyond 60 per cent relative humidity and no significant increase in swelling from 80 per cent relative humidity to saturation. It is suggested that a probable explanation could be the use by Speakman and Saville of filaments which had not previously been stabilised to water and in which, therefore, contraction occurred at high humidities offsetting the increased swelling

9. Volume Swelling and Lateral Swelling

From a knowledge of the density and regain properties of nylon, volume swelling can be readily calculated. Values for volume swelling can in turn be used in conjunction with longitudinal swelling data to derive information on the lateral swelling characteristics. Since the nylon filament is very close to circular in cross-section, where the degree of swelling is not large the percentage volume swelling is approximately equal numerically to the percentage longitudinal swelling plus twice the percentage lateral swelling.

A difficulty arises in the calculation of the volume swelling in water because of lack of precise knowledge of the saturation regain value. Linear extrapolation of the data for longitudinal swelling suggests saturation regain values for drawn and undrawn nylon in the region of 8·7 and 11·0 respectively. It is of interest to calculate the values for volume swelling and lateral swelling on the basis of these figures for saturation regain, and to compare them with results obtained by more direct observation. The values so calculated for saturation are included in Table VI along with data for relative humidities below 100 per cent.

Table VI

Relative Humidity (%)	Volume Swelling (%)		Lateral Swelling (%)	
	drawn	undrawn	drawn	undrawn
0 ...	0	0	0	0
10	0·6	0·7	0·2	0·3
20	1·0	1·3	0·3	0·5
30	1·7	1·8	0·5	0·6
40	2·4	2·4	0·8	0·6
50	2·9	3·1	0·9	0·7
60	3·4	3·9	1·1	0·8
70	4·2	4·7	1·3	0·9
80	5·1	5·9	1·7	1·1
90	6·2	7·6	2·0	1·4
95	7·0	8·9	2·3	1·6
100	8·1	11·0	2·6	1·9

The small magnitude of the lateral swelling in a single nylon filament prevented direct measurements of this swelling being made at various moisture contents. By using a projection microscope and an overall magnification of about 1500 times, it was possible, however, to obtain an approximate measure of the total swelling in passing from dryness to saturation. The average values obtained for this overall lateral swelling in water from about seventy measurements on each of several filaments were 2·6 per cent for the drawn nylon and 2·3 per cent. for the undrawn. The magnitude of the error of these values is reflected by the 95 per cent fiducial limits, which for the drawn filaments were ±0·9 per cent and for the undrawn ±0·4 per cent.

The correspondence between these admittedly rather uncertain values for lateral swelling in water and those shown in Table VI provides additional evidence that the saturation regain and swelling values suggested by the data on density and longitudinal swelling are not likely to be very greatly in error. The value of 11·0 for the saturation regain of undrawn nylon may perhaps be somewhat too low. Greater weight is also provided by these results in support of the view tentatively held that except in the low humidity range, longitudinal swelling in nylon filaments is closely represented as a linear function of regain right up to saturation.

In Fig 3 the volume and lateral swelling data of drawn nylon from Table VI are shown plotted against regain. Essentially similar curves result from the plotting of the data for undrawn nylon and need not be reproduced for consideration here The broken line has been drawn parallel to a line relating mass of water to its volume, when these quantities are expressed in the units used on the axes of Fig. 3. It has been made to coincide with the actual volume swelling curve at saturation regain The vertical distance separating the two lines is a volume difference, and at any regain may be considered as the volume of space within the fibre which water can progressively fill as the relative humidity increases The horizontal separation of the two at any regain shows immediately the weight of water which can be absorbed without being evidenced in swelling. This conception assumes, of course, that additional moisture accompanying that entering existing space causes swelling in an amount equal to its normal volume. The fact that the volume swelling curve is sensibly linear and departs from the broken line immediately below the point of coincidence at saturation, indicates that all the space which becomes available to water in the filament is not completely filled until saturation is reached. It may also be observed that of this total available space the proportion filled in the early stages of moisture absorption appears to be less for nylon than for silk or viscose rayon The rate of filling of the total space occupiable by water, together with the fibre density, influences the regain value at which maximum density occurs This follows from the fact that there will not be a decrease in density with moisture absorption until the addition of further moisture causes a swelling greater than the volume of the added moisture divided by the numerical value of the density of the filament.

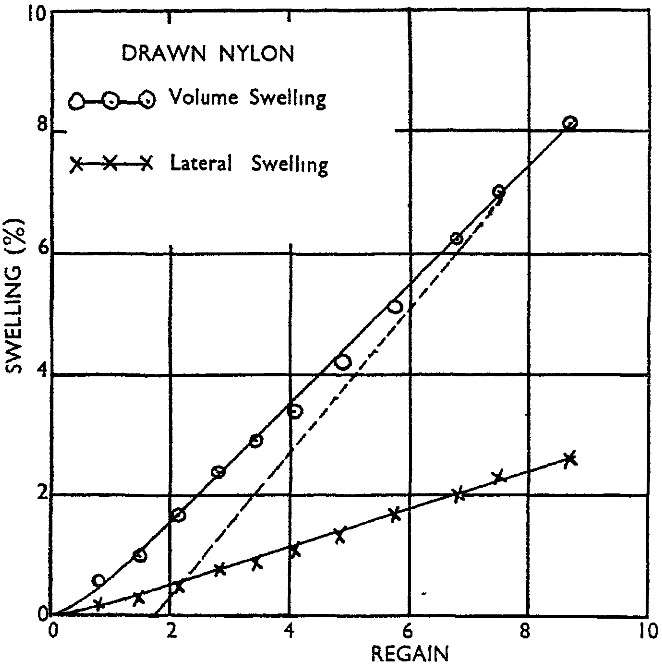

Fig 3

The intercept of the broken line in Fig 3 with the axis of zero swelling indicates the amount of water which will eventually enter into occupiable space In the case of drawn nylon this is 1·7 per cent of the dry weight of the filament, or 1·9 per cent of its dry volume Similar curves constructed from the data for undrawn nylon show the occupiable space in the filament to be 1 6 per cent. of its dry volume. These values show reasonably good agreement with those previously calculated in section 6 from true and apparent densities.

A striking feature of the results obtained on the swelling of nylon in water is afforded by a comparison of the percentage lateral and longitudinal swelling values. In the case of drawn nylon these are approximately the same, which in view of the highly oriented structure of the filament was totally unexpected In this respect also nylon differs from other textile fibres, in which the percentage lateral swelling is considerably greater than the percentage longitudinal swelling On the other hand the percentage longitudinal swelling in water of undrawn nylon is more than three times its percentage lateral swelling. This lateral swelling value appears to be somewhat less than for drawn nylon, while the percentage longitudinal swelling of undrawn is more than twice that of drawn nylon. No completely satisfactory explanation can as yet be offered for these results and the matter is receiving further study

10. Considerations of Space in a Nylon Filament

From the data given, an interesting calculation can be made of the intermolecular space present in a nylon filament in excess of that associated with a completely crystalline configuration Bunn and Garner[7] have estimated from their work on the X-ray diffraction patterns of nylon that the density of crystalline nylon is 1·24 g per c.c To account for the difference between this figure and the figure for the apparent density in water, namely, 1·166 g. per c c. for drawn nylon, an amount of empty space into which water cannot penetrate must be postulated. Complete penetration of the amorphous region would result in the two values being nearly the same; and in this connection P. H Hermans has shown for various cellulosic fibres an apparent density in water of approximately 1 61 against a crystalline density of 1 59 g per c c , indicating slightly more intimate contact of water with the cellulose molecules in the amorphous region than exists between neighbouring cellulose chains in a crystallite On the basis of a density of 1 24 g per c c for a packing equal to that in crystalline nylon, the additional space required to produce a density of 1·166 g per c c is 6 per cent. of the dry filament volume. This volume is space which water does not fill, and there is in addition approximately 1·8 per cent. accessible to water. On the assumption that space is not created during moisture absorption, 7·8 per cent of the fibre comprises space in excess of that present in the crystalline regions, of which space only 23 per cent. can be occupied by water. The value of 7 8 per cent for the total volume of space accords with a value of 7·7 per cent. calculated from a dry filament density of 1 145 and a crystalline density of 1 24 g. per c c. The assumption that space is not created during moisture absorption is therefore justified This volume being associated with the non-crystalline portion of the filament represents a higher percentage space in those regions. Certain evidence exists to indicate that the amorphous material in nylon comprises about 65 per cent. of the total fibre, in which case 12 per cent. of the amorphous region may be considered to be space Similar calculations for undrawn nylon give results which do not differ appreciably from those for drawn nylon. It is interesting that the greater proportion of the space in the filament remains inaccessible to water, and leads to speculation on possible arrangements of molecular chains which, without having a crystalline configuration, result in effective regional barriers.

SUMMARY

(1) The treatment of nylon with certain reagents has been shown to influence its moisture absorption properties in marked degree The amount of moisture absorbed can be either increased or decreased depending upon the reagent used

(2) The regains of drawn and undrawn nylon filaments have been determined for relative humidities ranging from dryness to saturation Drawn nylon filaments pre-treated with alcohol have similarly been studied for relative humidities up to 90 per cent Appreciable differences in the regain properties of these samples have been shown to occur only in the upper half of the relative humidity range· below 50 per cent relative humidity the regain curves for all three samples were found to be practically identical. Absence of any readily detectable hysteresis in moisture absorption by nylon previously wetted in water has been confirmed

(3) A contraction in the length of both drawn and undrawn nylon filaments on first wetting out with water has been shown to occur, and its magnitude investigated

(4) The densities of drawn and undrawn nylon filaments in equilibrium with relative humidities ranging from zero to 98 per cent. have been measured by a flotation method The apparent densities in water have also been determined.

(5) Measurements of longitudinal swelling of drawn and undrawn nylon filaments have been carried out for conditions ranging from dryness to saturation (immersion in water). Volume swelling values have been calculated from density data, and lateral swelling has been computed from the corresponding figures for the volume and longitudinal swellings Values for lateral swelling in water have also been attempted by direct measurement of magnified images of filaments, and the results, while of a low order of precision, support the finding of the other experimental data The longitudinal and lateral percentage swellings in a drawn nylon filament have been found to be approximately equal, but in undrawn nylon the longitudinal swelling has been shown to be three times the lateral swelling.

(6) The volume of empty space in a nylon filament has been computed from the experimental data, and it has been shown that a major portion of this volume is not penetrated by water even at saturation

ACKNOWLEDGEMENT

The authors wish to express their thanks to Canadian Industries Limited, Nylon Division, who sponsored the work and gave permission for the results of the investigation to be published

REFERENCES

[1] Speakman and Saville *J Text Inst*, 1946, 27, P271
[2] Data from *International Critical Tables*
[3] White and Eyring *Text Res. J*, 1947, 17, 523
[4] Bergman, Fankuchen, and Mark *Text Res J*, 1948, 18, 1
[5] P H Hermans "Contributions to the Physics of Cellulose Fibres" Elsevier 1946.
[6] Goodings and Turl *J Text Inst*, 1940, 31, T69
[7] Bunn and Garner *Proc Roy Soc A*, 1947, 189, 39

Toronto, Ontario

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Letters to the Editor

[The Institute is not responsible for the opinions of correspondents.]

A Suggested Method of Testing Woven Fabrics for the Measurement of Resistance to Slippage of Warp Threads over the Weft, or Weft over Warp

On making a survey of the fabrics produced today, as against those produced twenty-five or thirty years ago, a very marked change is apparent. The old setting theories put forward by technologists in the Victorian period appear to have become out of date and are entirely disregarded In consequence, new features and styles have been introduced into modern design and production of materials.

It is apparent that the qualities now demanded in modern fabrics are that they be elegant in appearance, soft and supple in handle, and possess special draping qualities With these qualities ever in the producers' minds, fabrics are now made to comply with these requirements In fact, some of the modern fabrics are so loosely constructed that they do not possess the requisite cohesion of warp and weft, and, as a consequence, are very susceptible to slipping or fraying

The necessity for the introduction of non-slip treatments on fabrics confirms this and shows that some of the structures produced today require additional assistance before the materials are in a satisfactory condition to be used in the industry. We are therefore faced with the urgent problem of how textiles can be tested to show their relative merits in respect to resistance to slippage

This matter of testing for the degree of slip or distortion by the slippage of warp threads over weft, or *vice versa*, is of paramount importance, and it is with this need in mind that a careful examination into the problem of how best to ascertain the measure of resistance to slip has been instituted.

In 1935, the A S.T M [1] published a proposed method of test for Slippage in Silk and Rayon Woven Broad Goods, and at that time they appealed for suggestions as to how this property of resistance to slippage could be measured It appears that up to 1942 no further suggestions or improvements had been accepted, and therefore they proposed a standard test for the measurement of resistance to slippage by means of seam testing, Designation D434/42.[2]

In this country the above method has been used fairly extensively, in domestic concerns for their own internal research purposes, but whilst seam testing has many good points, the information obtained can be acceptable and reliable only if the work is conducted by one person Standardisation of this type of testing may therefore be very difficult, because in practice the work has to be done in many laboratories with the employment of entirely different apparatus and personnel

The preparation of the samples in a uniform or standard manner is not by any means as easy as it appears at first sight Even slight variations in the preparation of the seams unquestionably may have a very marked influence on the results obtained.

In the writer's opinion, there are many technical difficulties which could have a most serious effect on the test results, even thought the tests may superficially appear to have been carried out strictly in accordance with the prescribed method. For example, needle damage and the gripping or binding properties of the stitching material used may vary enormously, although these variations are not apparent on normal visible examination

It is the writer's experience that complaints in the industry regarding slippage or fraying are by no means confined to the slippage at the seams only, and further, when such complaints on seam slippage are examined, it is very frequently found that the seams concerned are not those made parallel to either warp or weft, but those made on the bias and with insufficient overlap. These conditions put an entirely different complexion on the material's serviceability, and also on the relative value of the seam tests carried out as prescribed in the American Standards Designation D434/42.

It is therefore the object of this new testing method to attempt to eliminate the complications associated with stitching seams and place before the industry a simpler and more easily controlled method of ascertaining the resistance to slippage of the fabric, entirely divorced from seams and seam testing. By this new method of test, the merits of the fabric are being measured to ascertain the cohesion of the warp and weft, and not with reference to the serviceability of a seam or with the efficiency of making seams.

It is therefore suggested that the investigation into the technicalities involved in the making of satisfactory seams in garments should be treated as a problem entirely separate from that of the resistance to slippage of a fabric.

PROPOSED METHOD OF TEST TO ASCERTAIN THE MEASUREMENT OF RESISTANCE TO SLIPPAGE OF FABRICS

Scope. This method of test applies to the measurement of the resistance to slippage of warp threads over weft or weft threads over warp in woven fabrics, it being specially suitable for those fabrics which are so constructed as to be susceptible to slipping or fraying.

Slippage. The resistance to slippage is the pull (expressed in pounds or kilogrammes) necessary to produce a movement of warp threads over weft threads, or *vice versa.*

Apparatus. The tests shall be carried out on any approved tensile strength testing machine (constant rate of load type preferred, with the rate of load fixed at 40 lb. per minute) and using a specially constructed adaptor. This adaptor is in two parts:—

(1) The base plate, which is designed to fit vertically into the pulling jaw of the approved testing machine.

(2) A specially designed and constructed pin setting, which slides horizontally into the base plate. The pin settings have been standardised and are being produced in two types, one for use when testing coarse fabrics, and a finer setting for use when testing medium and fine set cloths The pins, which are made of stainless steel and are of standard shape and thickness, are set into the brass slide as follows:—

For the fine setting, 32 pins at $\frac{1}{16}$ in pitch.
For the coarse setting, 16 pins at $\frac{1}{8}$ in pitch

The pins are set in the slide at 5° to the horizontal and pointing downwards.

Preparation of Test Specimens

Five test specimens in each direction shall be prepared by cutting to 2½ in wide and fraying down to 2 in , leaving ¼ in. fringe at each side

The length of the specimen shall be such that it will allow the operator to have sufficient material to mount it, evenly tensioned, in the machine or on a mounting jig.

One end of the specimen shall be cut parallel to the threads which have to be frayed out From this end, a mark ¼ in from the edge shall be made, and it is on this line that the specimen shall be pressed, gently and evenly, on to the pin setting

Care must be taken to place the specimen evenly and squarely on the pins, and this is facilitated by using a piece of cork or rubber

The other end of the test specimen is carefully and evenly secured in the top jaw of the tensile strength machine The distance between the pin setting and the top jaw shall be 4 in.

Conditioning of Test Specimens

All specimens shall be conditioned for a prescribed period in accordance with B S 1051/1942, and tested without removal from these conditions.

Having the specimen satisfactorily mounted in the tensile strength machine, the load is then applied When the first sign of slippage is observed the load is noted The straining is continued until the crossing threads are slipped entirely out, and the total load applied is then recorded. In most fabrics the first slippage is readily seen, but by using a stress strain recorder the chart produced is of exceptional value.

A load/elongation curve made of the material in the form of a tensile strength test as compared with the slippage chart is of paramount importance The size of the specimen used for the tensile strength test would of course be 2 in. wide and 4 in in length between the jaws

By this method of test one can ascertain accurately when a fabric first slips, and also the necessary force required to slip out of the fabric a defined number of crossing threads.

In very coarse fabrics it may be advisable to make the insertion of the pins at a greater distance from the prepared edge, and in such cases useful data have been obtained by making tests at varying specified distances from the edge of the pattern.

This principle of pulling out of a fabric one series of threads by means of this pin setting has proved to be a very useful method of obtaining data when investigating certain irregularities relating to the breakdown in the serviceability of fabrics

For such special research purposes it has been found an added advantage to apply this principle in varying forms in order that the test may more nearly coincide with the type of defect being investigated.

It is with this purpose in mind that the following additional pin settings have been produced:

16 pins set at $\frac{1}{16}$ in pitch.
8 ,, ,, ,, $\frac{1}{16}$ in ,,
8 ,, ,, ,, $\frac{1}{8}$ in ,,
4 ,, ,, ,, $\frac{1}{8}$ in ,,

Fig. 1 illustrates the pin setting slide in its correct position in the adaptor, that is, with the pins pointing downwards. The setting of the pins in this special manner is to ensure that during the testing the fabric is kept close up to the base plate.

When mounting the specimen, care is required to make sure that the material is pressed squarely and evenly on to the pins in the base plate, and it is found an advantage to keep the cork or rubber used for this purpose on the pins until the operator is ready to make the test

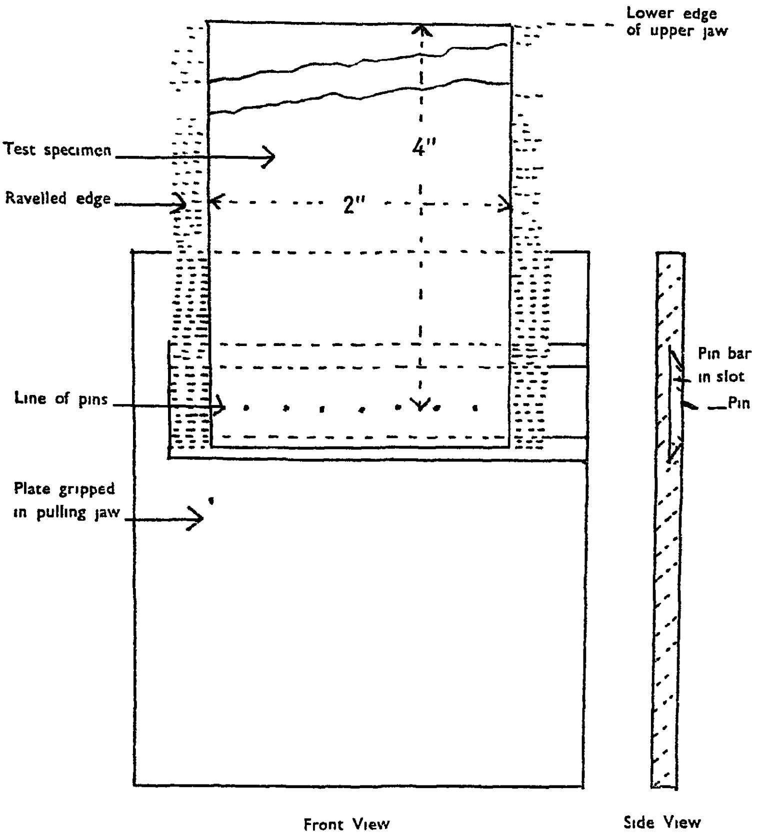

Fig 1

Adaptor used in measuring resistance to slip .

It has been stated previously that the use of a stress-strain diagram clearly records the behaviour of the fabric under this new test, and the two charts reproduced show the difference of the slippage of the fabric when strained in the warp or weft direction

Curve A is the load-elongation diagram obtained when making the ordinary tensile strength test carried out on a Constant Rate of Load Tensile Strength Machine (rate of load 40 lb per minute)

Curve B records the behaviour of the fabric when making this new test

It will be readily noticed that Curve B contains many serrations which graphically exhibit the periods of slippage The value of these serrations is most important in assessing the slippage potential of the fabric

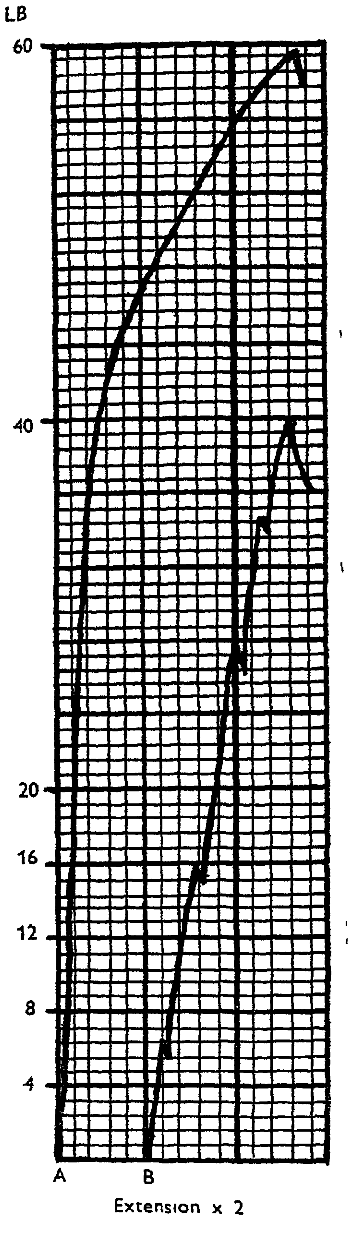

Fig. 2 Warp strip

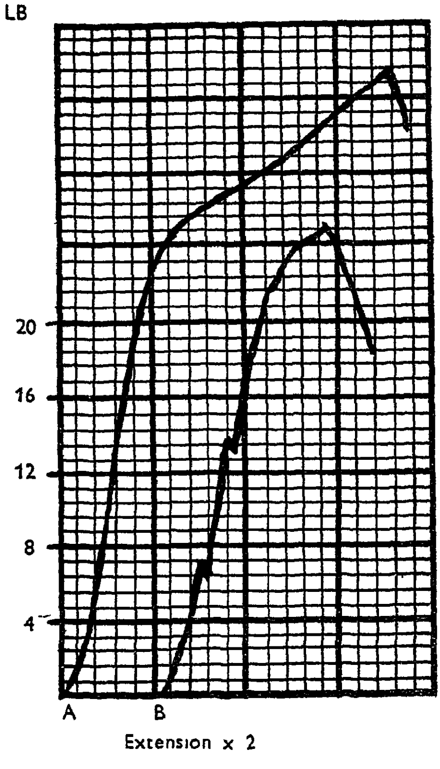

Fig 3 Weft strip

It will be noticed that in the American Seam Testing Specification D434/42, Note 6 states "If the load-elongation curve is serrated, a smooth curve shall be drawn through the tips of the serrations" By producing a regular curve, the significance of the yielding of the fabric due to slipping is lost, and also a considerable amount of the value of the test.

ACKNOWLEDGEMENT

The author wishes to acknowledge the assistance of Mr F. Ibbetson of the Bradford Conditioning House in providing facilities for undertaking tests in connection with this paper.

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REFERENCES

[1] A S T M Standards on Textile Material, 1935, 214.
[2] A S T M Stnndaros on Textile Material, 1941, 277.

Erratum

It is regretted that the name of Mr Chadwick was omitted from the contents panel on the cover of the Transactions Section of the February *Journal* Mr Chadwick's name should have preceded those of Dr. Shorter and Dr. Weissenberg.

THE JOURNAL OF THE
TEXTILE INSTITUTE

TRANSACTIONS

15—A SIMPLIFIED SLIVER TESTER

By J. U. Steiger

SUMMARY

A machine is described by which variations in the thickness of cotton slivers are mechanically measured and charted. Greater dimensional tolerance is permissible than in previous designs, resulting in a relatively low cost of manufacture. Examples of the use of the machine in detecting sliver faults are given.

Purpose of Machine

It is well recognised, and is indeed self-evident, that the successful use of short processing in cotton spinning requires the drafting mechanism of the drawframe to be in good mechanical condition and correctly adjusted, owing to the elimination of the doublings which previously served to correct drafting irregularities. Thus in spinning medium counts from single roving, while there were four doublings after the drawframe in the old process using three speed frames, in the modern system embodying one high draft speed frame there are none, any hank variation present in the finisher sliver is therefore reproduced in the yarn, with variation of later origin superimposed. Such variation can result in considerable loss of production and impair the morale of the operatives if not soon detected and rectified. An example may be cited in which the use of eccentric pinions on certain drawframes produced a periodic variation in hank recurring every two feet along the sliver. Though this had no effect on the lea strength or blackboard appearance of the yarn, it caused an increase of 100 per cent. in the end breakage rate at the ring frame, to overcome which a 15 per cent. reduction in spindle speed was necessary until the fault was corrected.

In cases such as the above it is not usually possible to detect by eye the existence of periodic variations in the sliver or to measure the length of the period. A cutting and weighing method can be used but the time required prohibits its use except on a small scale. To check many samples of sliver for regularity requires the use of a sliver testing machine which will draw a graph of the variation in thickness along the sliver. Such an instrument has been described by Foster and his co-workers, of the British Cotton Industry Research Association[1], in which the sliver being tested is drawn between two wheels, variation in thickness of the sliver causes a corresponding variation in separation of the wheels which is magnified and recorded photographically. A machine working on the same principle, the Saco-Lowell Sliver Tester, is commercially available in the U.S.A., though in this case the recording is done by means of a pen.

Instruments of this type, though capable of great accuracy are inevitably rather costly, since great precision is required in the manufacture of the wheels and their mountings. The present paper describes a mechanical sliver testing machine designed with the objects of simplicity and the avoidance of unusual accuracy in manufacture The cost of manufacture was approximately £60

Principle

The measuring unit of the machine consists essentially of a sliver condensing trumpet. These trumpets, in which there has been considerable recent interest, are used on drawframes to compress and condense the sliver. This is effected by means of a reduced aperture, set at a distance from the calender roller nip not exceeding the staple length of the cotton, this is necessary since the considerable force required to pull it through the aperture would otherwise rupture the sliver. Fig 1 shows a cross section through the unit.

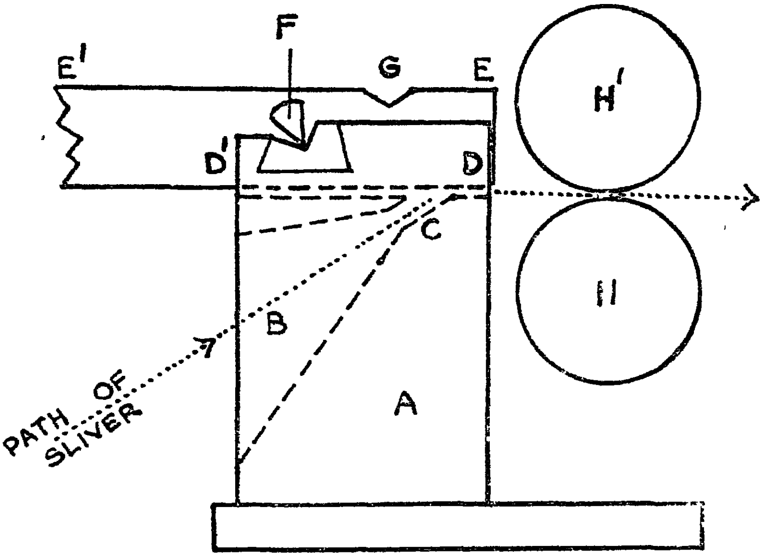


Fig 1 Diagram of measuring unit (full size)

A rectangular block of metal A has machined in it a conical hole B tapering to a cylindrical throat C of $\frac{1}{8}$ in. diameter, which is drilled through the bottom of a rectangular slot DD', $\frac{1}{8}$ in wide, cut in the top of the block A lever EE', $\frac{1}{8}$ in wide and pivoted on a knife edge F, closes the top of the slot, and is held in place by a weight of 8 lb suspended by a knife-edged weight hook from a notch G A pair of fluted rollers HH', set at a distance from the block of less than the staple length of the cotton likely to be used, draws the sliver through the block without slip and without appreciable stretch Variations in thickness of the sliver cause variations in the aperture of the trumpet by moving the end E of the lever EE', which pivots about the knife edge F. The movement of the other end of the lever is picked up, magnified and recorded on a drum driven by the roller H

The lever fits in the slot with a clearance of 0 008 in , which cannot be considered excessively precise

Construction

The machine is built on a base consisting of a length of 5 in channel section carried on a tubular tripod at a height sufficient to allow the can of sliver to be placed underneath The sliver passes up through the hole in the base, through the block and is discharged by the rollers onto the floor

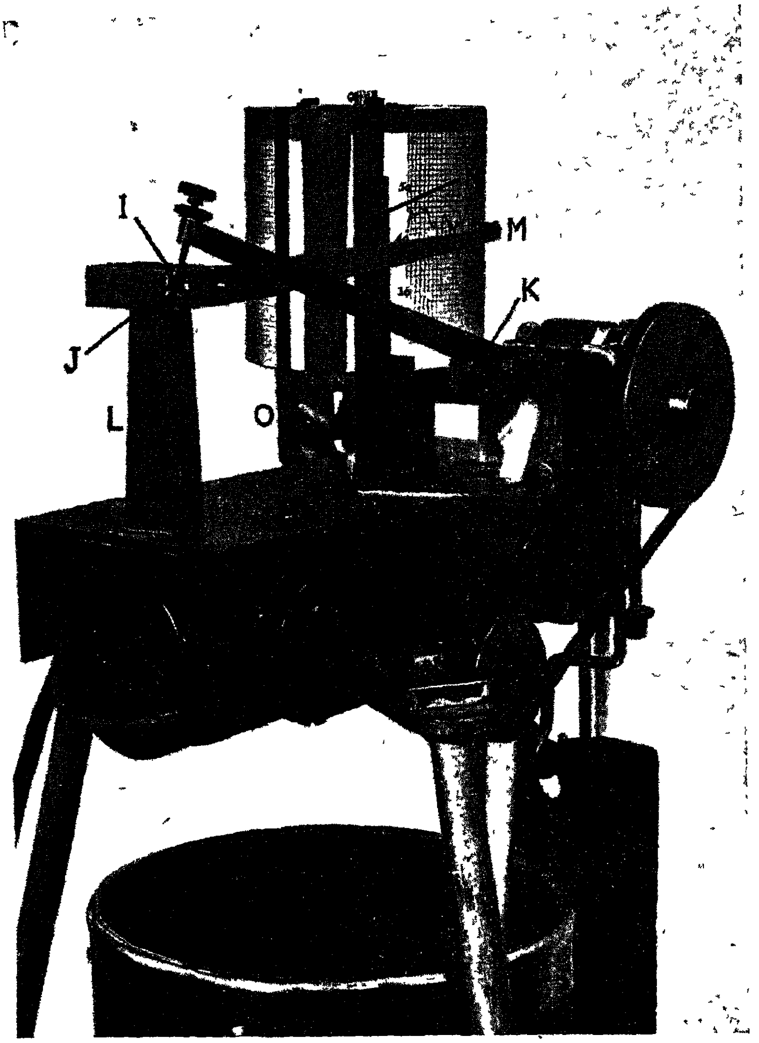


Plate I Detailed view

The block lever EE′ (Fig 1) is provided at its end with an adjustable shoe I (Plate I) which bears against a point J on the shorter arm of the magnifying lever An additional adjustment in the form of an articulation on the block lever is provided at K should the range of movement of the shoe I prove insufficient. The magnifying lever pivots about two points carried by the post L and has a longer arm of spring steel carrying the pen M. Each of the two levers has a shorter arm of 1 in and a longer arm of 10 in , thus the movements of the end E of the block lever in opening or closing the aperture of the trumpet are magnified one hundred times by the pen. A device N is provided to lift the pen from the chart when required

The fluted rollers HH′ of 1 in diameter are carried on sideplates fixed to the sides of the block, and are geared together The top roller works in a slot with a weighting of 20 lb applied through weighthooks, which is sufficient to prevent any slip The drive is taken through a flexible connection to a wheels and their mountings The present paper describes a mechanical sliver testing machine designed with the objects of simplicity and the avoidance of unusual accuracy in manufacture The cost of manufacture was approximately £60.

Principle

The measuring unit of the machine consists essentially of a sliver condensing trumpet These trumpets, in which there has been considerable recent interest, are used on drawframes to compress and condense the sliver. This is effected by means of a reduced aperture, set at a distance from the calender roller nip not exceeding the staple length of the cotton, this is necessary since the considerable force required to pull it through the aperture would otherwise rupture the sliver Fig 1 shows a cross section through the unit

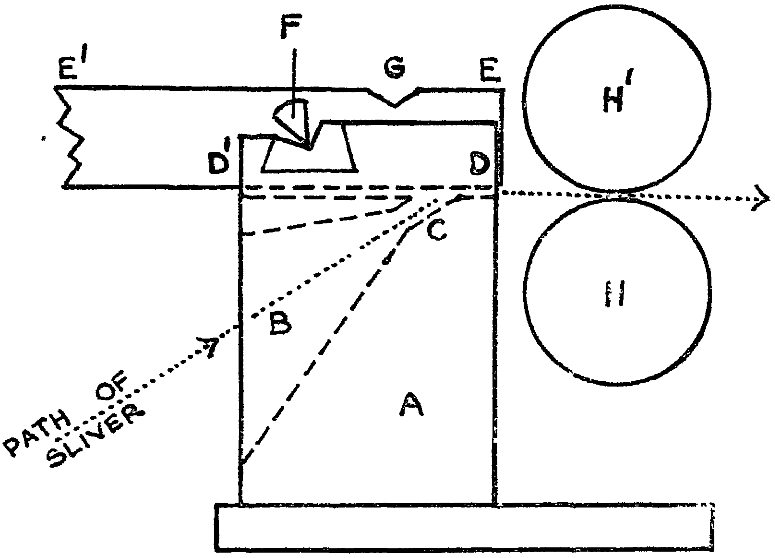


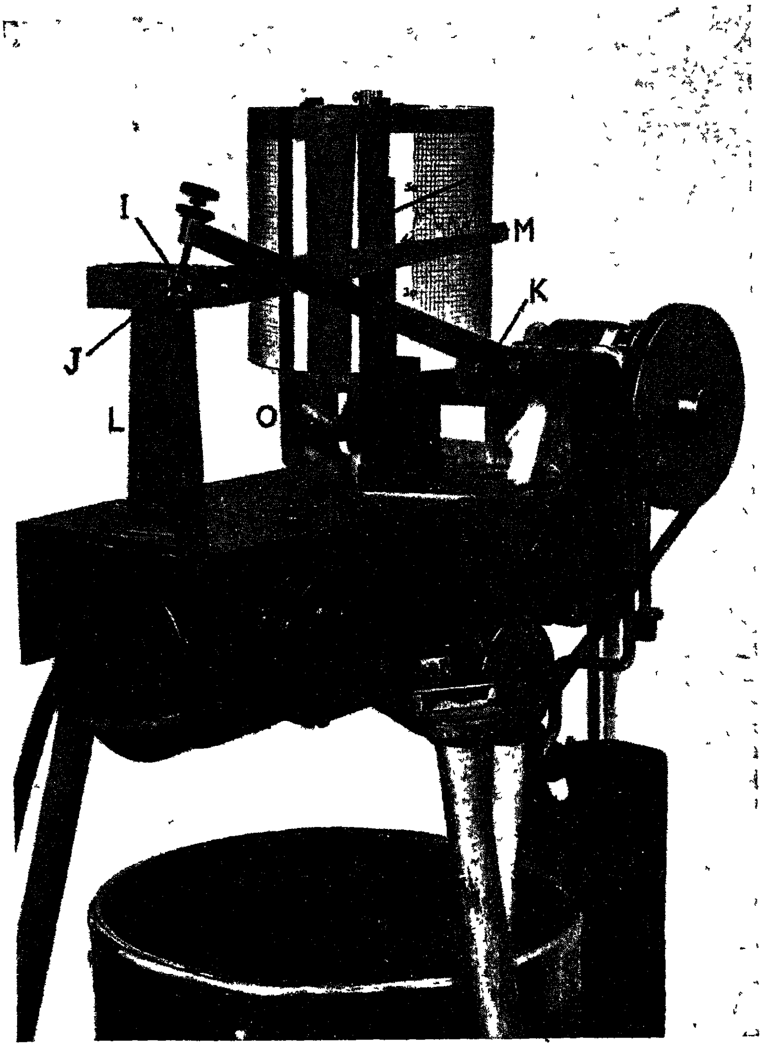
Fig 1 Diagram of measuring unit (full size)

A rectangular block of metal A has machined in it a conical hole B tapering to a cylindrical throat C of $\frac{1}{8}$ in diameter, which is drilled through the bottom of a rectangular slot DD', $\frac{1}{8}$ in wide, cut in the top of the block A lever EE', $\frac{1}{8}$ in wide and pivoted on a knife edge F, closes the top of the slot, and is held in place by a weight of 8 lb suspended by a knife-edged weight hook from a notch G A pair of fluted rollers HH', set at a distance from the block of less than the staple length of the cotton likely to be used, draws the sliver through the block without slip and without appreciable stretch Variations in thickness of the sliver cause variations in the aperture of the trumpet by moving the end E of the lever EE', which pivots about the knife edge F The movement of the other end of the lever is picked up, magnified and recorded on a drum driven by the roller H

The lever fits in the slot with a clearance of 0·008 in , which cannot be considered excessively precise.

Construction

The machine is built on a base consisting of a length of 5 in channel section carried on a tubular tripod at a height sufficient to allow the can of sliver to be placed underneath The sliver passes up through the hole in the base, through the block and is discharged by the rollers onto the floor



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The fluted rollers HH′ of 1 in diameter are carried on sideplates fixed to the sides of the block, and are geared together The top roller works in a slot with a weighting of 20 lb applied through weighthooks, which is sufficient to prevent any slip. The drive is taken through a flexible connection to a

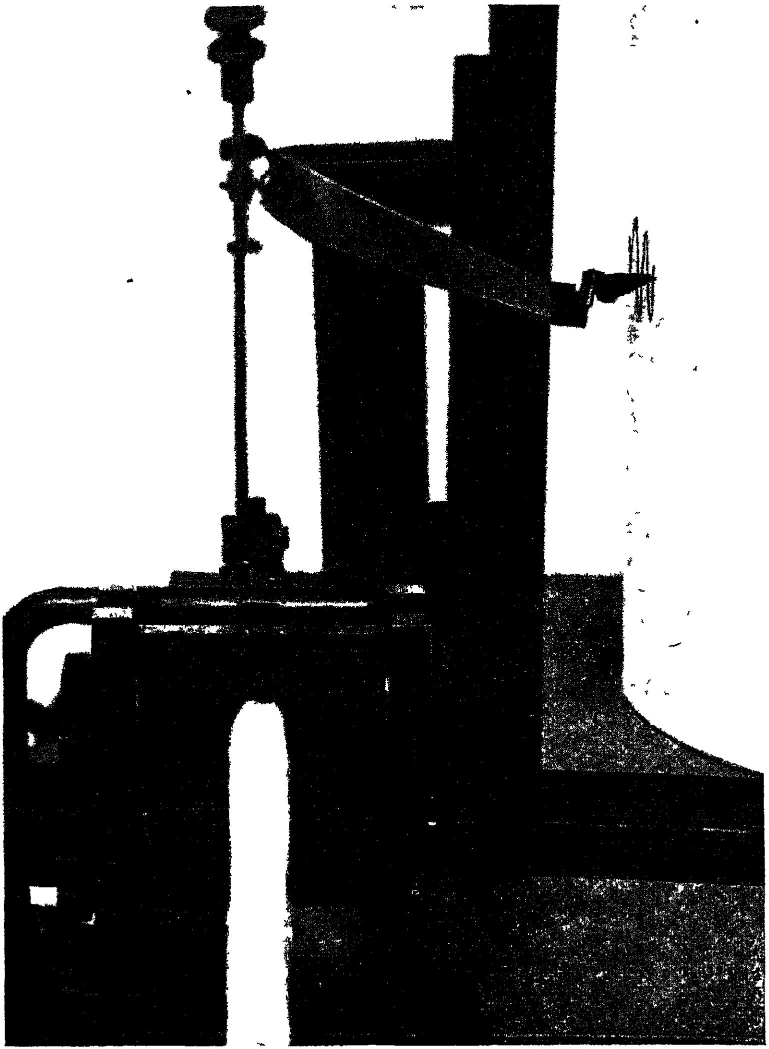

Plate II View with top roller removed, showing sliver issuing from slot block lever and weight hook

two speed gearbox O, made up of Meccano 50 tooth gears and single worms, which is diagrammatically illustrated in Fig 2 The change in speed is effected by loosening the set screw of gear P with a screw-driver through a slot on the side of the gearbox and moving the gear on its shaft into mesh with one or other of two worms

The gearbox drives the recording drum Q, which is 5 in in diameter and 5 in high at either 1/50 or 1/2500 of the fluted roller speed Making allowance for the difference in diameter between the fluted roller and drum diameters the two speeds are equivalent to scales of 10 in and 500 in of sliver to an inch of paper respectively

The machine is driven by a fractional horsepower gear motor placed underneath the base, which draws the sliver through the machine at the rate of 5 feet per minute. This is a convenience for testing long lengths of

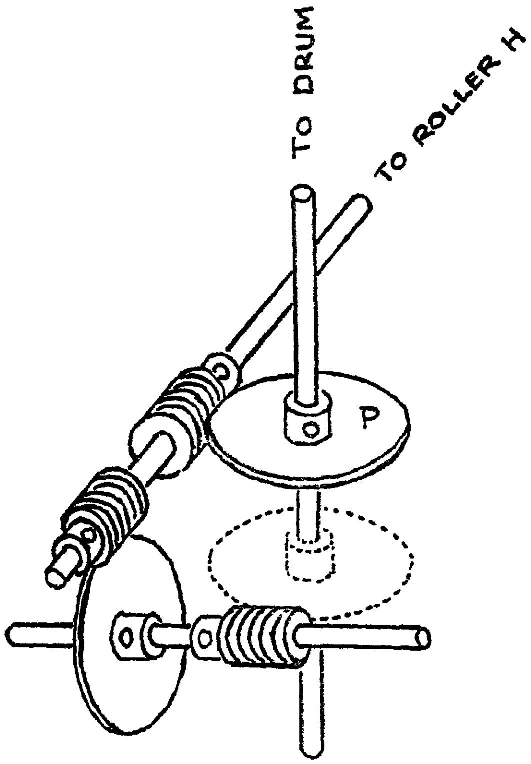

Fig 2 Diagram of 2 speed gear box

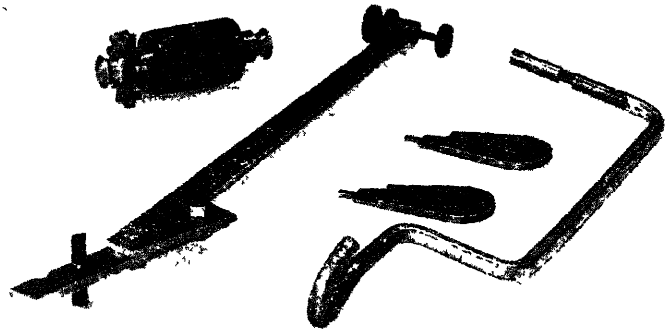

Plate III Details of fluted top roller, block lever, gauges and block lever weight hook (showing knife edge)

sliver, though good results were also obtained with a hand drive provided the speed was not excessive

Calibration

The dimensions were chosen so that the drum would take half a sheet of foolscap graph paper bisected lengthways Paper divided in inches and tenths is used, one division along the chart representing 1 in or 50 in of sliver and the whole chart recording 3½ or 180 yards of sliver depending on the drum speed Each division across the chart represents one thousandth of an inch opening of the aperture, the zero, however, usually lies off the paper, and is adjusted by the shoe I so that the record lies centrally

In order to calibrate the chart before a test one of the gauges R, of appropriate thickness depending on the hank of the sliver, is inserted in the aperture, with the top roller removed, and the shoe I is adjusted until the pen lies on a convenient chart line, when the shoe is locked with the lock unit The value of one line being known that of the remainder can be written in By this means the variations in thickness plotted on the chart can be transformed into a coefficient of variation or other appropriate measure if required

The relationship between the thickness and the hank of the sliver was investigated for card sliver and for finisher drawframe sliver in the following manner A series of three card slivers and another of seven drawframe slivers were prepared varying in hank by suitable steps Six yards of each sliver were measured off on a wrap block and weighed, from which the mean hank over the six yards was ascertained The six yard length was then passed through the machine at the slow drum speed, and the mean thickness ascertained from the trace by inspection The ten traces are shown in Fig 3, the numerical results being as follows —

Origin	Sliver	Hks/Lb	Lb/Hk	Estimated thickness 1/1000 in
Card	A	0 193	5 19	59 0
,,	B	0 152	6 58	70 5
,,	C	0 126	7 94	83 5
Drawframe	D	0 314	3 18	28 0
,,	E	0 253	3 96	36 0
,,	F	0 210	4 76	43 0
,,	G	0 179	5 59	50 5
,,	H	0 157	6 37	58 0
,,	I	0 138	7 25	64 5
,,	J	0 124	8 07	72 0

From these results, which are plotted in Fig 4, it is seen that a linear relationship exists between the weight per unit length of the sliver and its thickness, as measured by the machine in the case of both card and drawframe slivers Card sliver appears thicker than drawframe sliver of the same hank, doubtless due to its less oriented character, and the line does not pass through the origin as is the case with drawframe sliver The difference between the two types of sliver though of interest theoretically, has little practical importance in the utilisation of the machine

Reproducibility

Since the sliver is not damaged in passing through the machine repeat tests may be made on any sample if required Fig 5 shows the original and a repeat test made on the same length of finisher drawframe sliver, the zero of the repeat test was moved to separate the two graphs. Despite a few local differences, the correspondence is striking. By measuring between corresponding features of both curves, it is seen that the sliver was stretched only 1 per cent. during the repeat test.

Comparison of Card, First and Second Head Sliver

Fig. 6 shows the results of tests on a group of drawframes making 0·21 hank finisher sliver from 0·15 hank card sliver in two passages with roller settings of 49, 53, and 61 thirty-seconds of an inch from front to back. The cotton was American of effective length 39 thirty-seconds.

It is seen that over the short lengths covered by the charts at the faster drum speed, the card sliver is the most regular product, but that it contains long period variations, doubtless due to the scutcher laps, which are revealed only when long lengths are tested at the slower drum speed. These long period variations are absent in the drawframe slivers.

Drawframe Faults

Charts made at the higher drum speed from faulty drawframe sliver usually, though not always, show a regular periodicity, the length of the period depending on the cause of the fault. Thus a faulty back roller of $1\frac{3}{8}$ in. diameter at a draft of 6 would be expected to produce a period of 26 in., which is the length of sliver delivered by the drawframe for one revolution of the faulty roller. The period can be determined from the chart by inspection with sufficient accuracy to suggest the location of the fault.

In the investigation of faults and in routine checks it is advisable to test every delivery of a drawframe. This allows for a more accurate determination of the period if the fault is present in all the deliveries, as is often the case, and there is less chance of its being concealed by casual variation as may happen if only one test is made on the frame. The fact that the fault is or is not present in all deliveries is also a valuable clue to its identity.

The following are examples of faults located in this way.

Figs. 7 and 8 show the effects of bent steel rollers. The bend usually occurs in the neck at the gearing end and the fault is easily seen in the eccentric running of the roller end pinion. This fault appears relatively common with the make of drawframe concerned and raises the question whether the rollers are sufficiently supported against the forces produced by the gearing.

The faulty sliver in Fig. 9 was made with a second roller pinion which had been bored eccentrically, this pinion had probably at some time had its bore enlarged carelessly by filing. The fault was easily seen with the pinion revolving.

In Fig. 10 is seen the result of failure to buff the cork top rollers frequently enough, they had been running about eighteen months since buffing and had worn slightly hollow. The fault has been encountered only in connection with front top rollers, exchanging the faulty rollers between the different lines showed that the second, third and back lines were insensitive to this degree of hollowness.

A broken front roller stand caused the fault shown in Fig. 11, the rear arm having broken off, thus releasing the constraint from one end of the top roller. Such breakages are the result of front top roller laps being allowed to build up by a badly set electric stop motion.

If the weight hooks are incorrectly set it is possible for the weight relieving motion, though in the inoperative position, to take the weight off the roller, and Fig. 12 shows an extreme case of this in which the second top roller was involved This variation could easily been seen in the sliver, though in fact it passed unnoticed.

ACKNOWLEDGEMENTS

The author is indebted to the Directors of Messrs James Williamson and Son Ltd , Lancaster, for permission to publish this paper, and to their Engineering Dept for the construction of the machine.

REFERENCES

[1] Anderson, Cavaney, Foster and Gregory *J Text Inst*, 1945, 36, T 191

Lancaster
6th August, 1948.

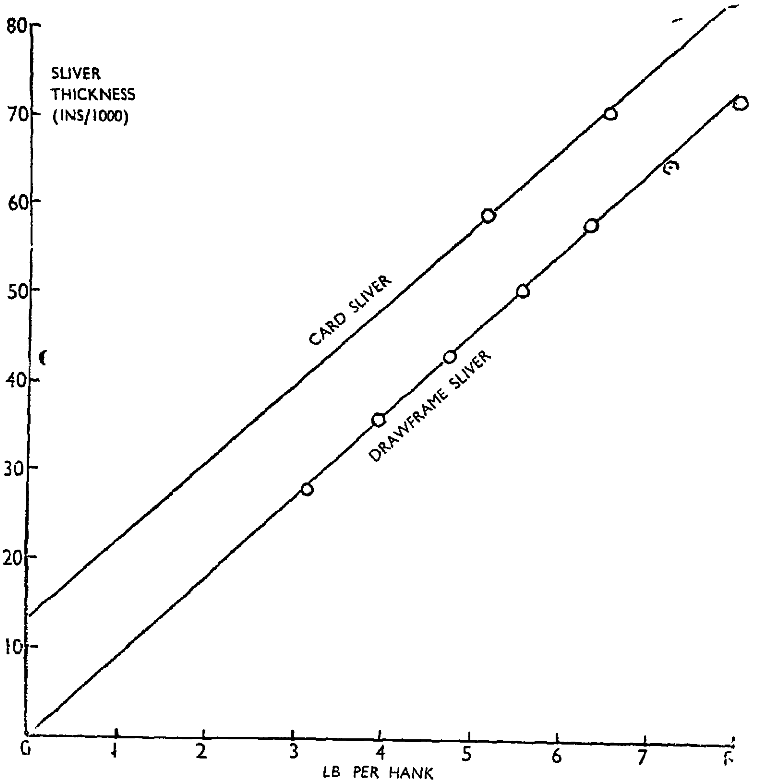

Fig 4 Thickness and weight of slivers

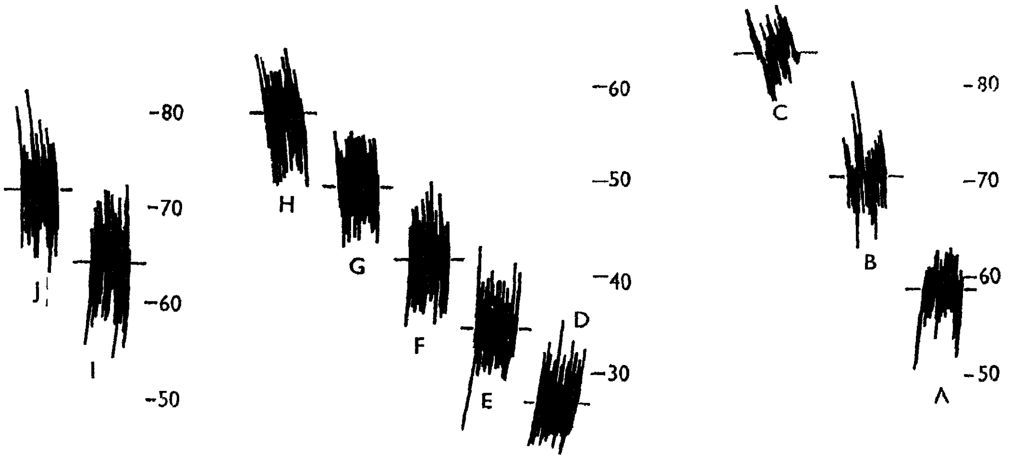

Fig. 3
Calibration curve

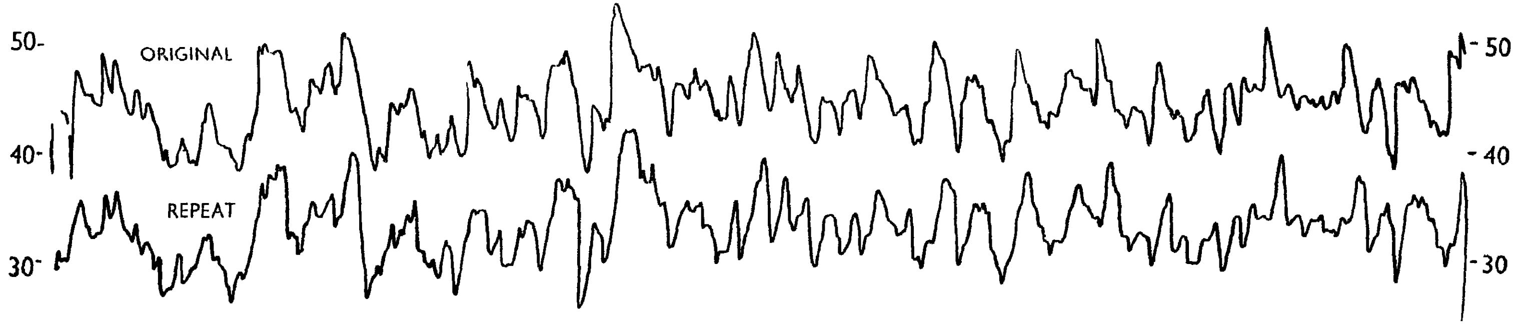

Fig 5. Two tests on same length of sliver 0·21 Hk, DF24/3, 4/8/48.

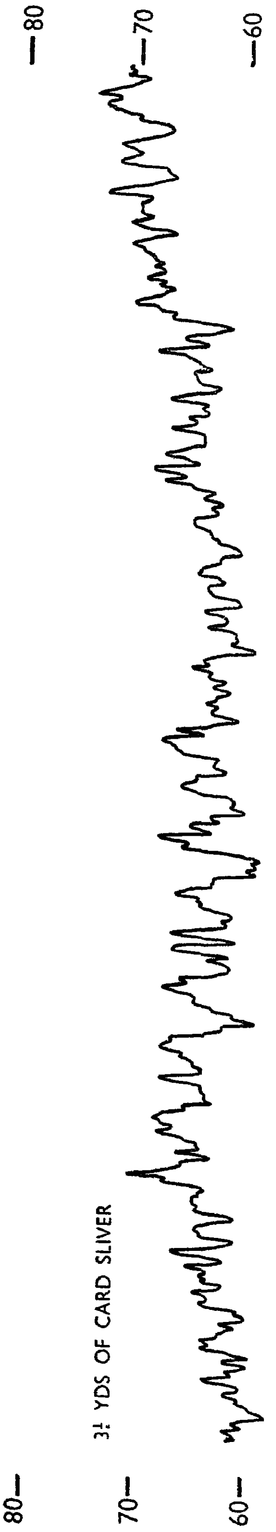
80
70
60
3½ YDS OF CARD SLIVER
80
70
60

Fig 6 (*a*)

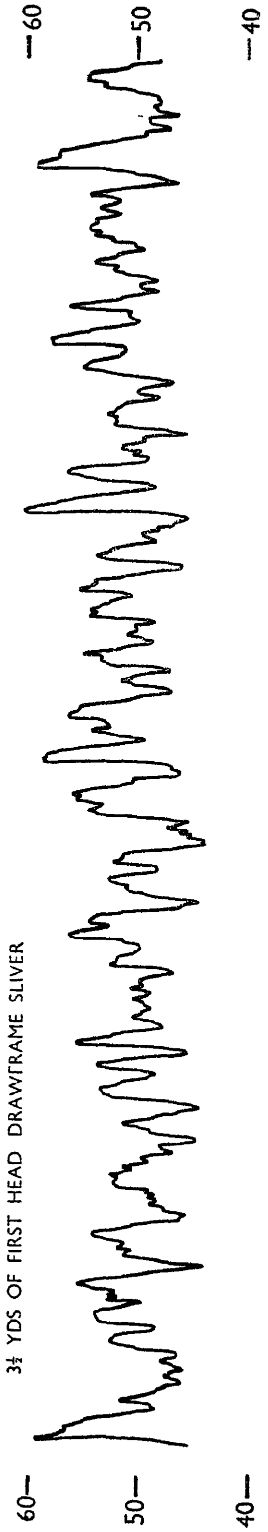
60
50
40
3½ YDS OF FIRST HEAD DRAWFRAME SLIVER
60
50
40

Fig. 6 (*b*)

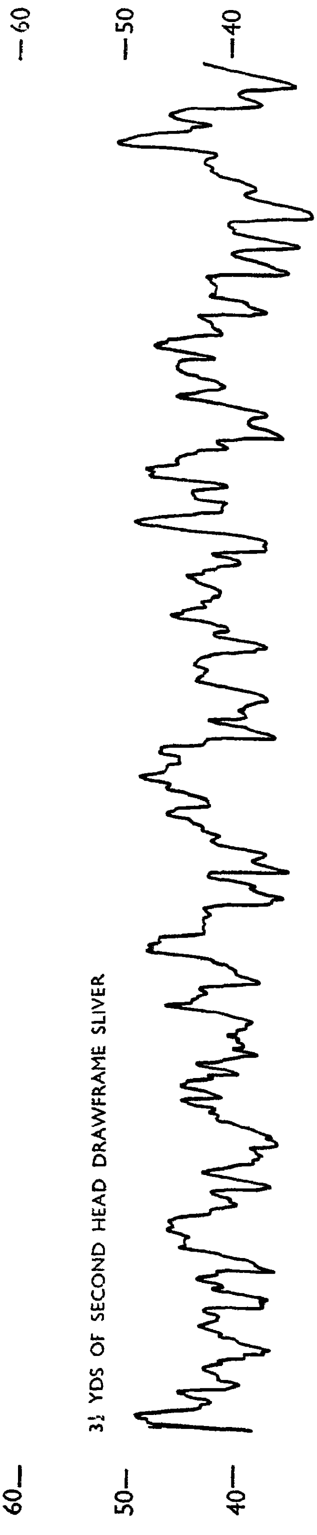
3½ YDS OF SECOND HEAD DRAWFRAME SLIVER
60
50
40
60
50
40

Fig. 6 (*c*)

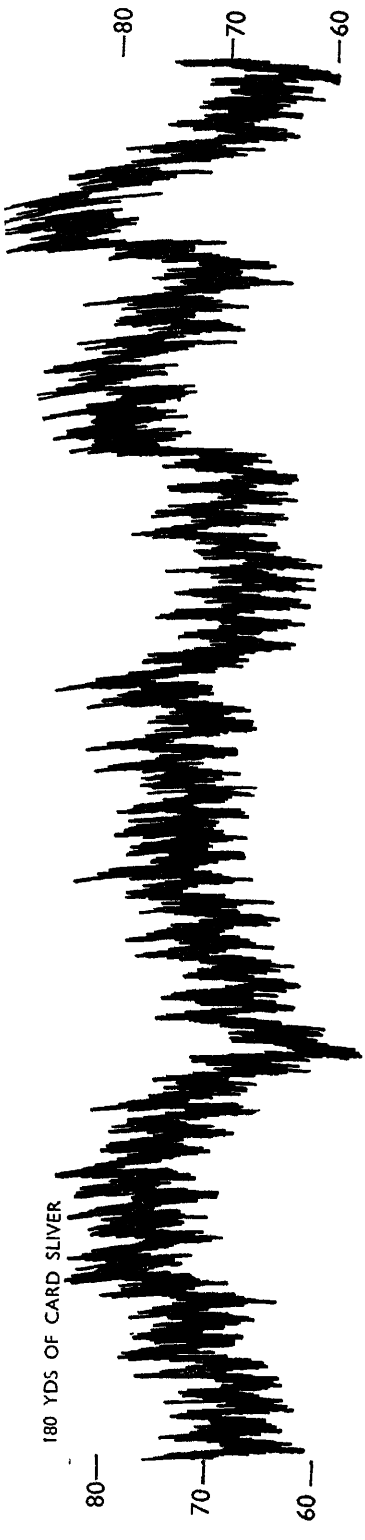
180 YDS OF CARD SLIVER
80
70
60
80
70
60

Fig. 6 (*d*)

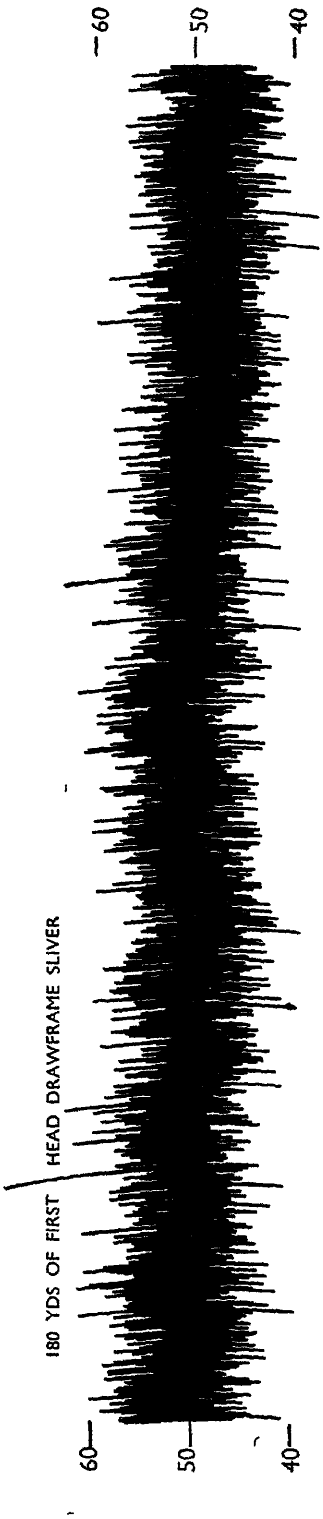
60
50
40
180 YDS OF FIRST HEAD DRAWFRAME SLIVER
60
50
40

Fig. 6 (*e*)

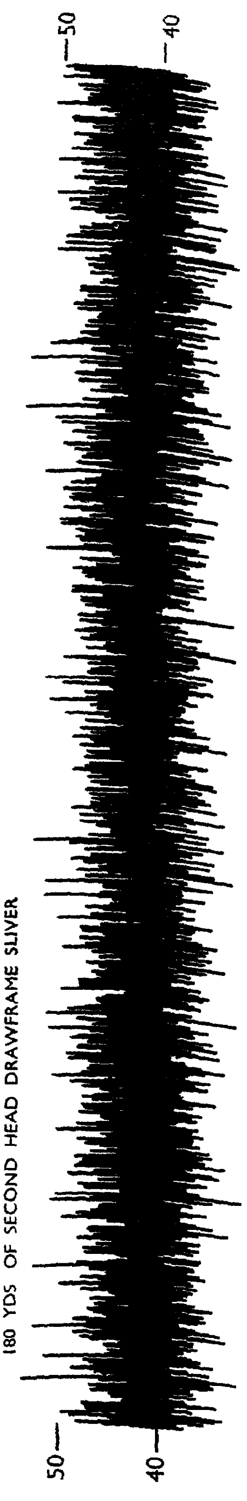
60
50
40
180 YDS OF SECOND HEAD DRAWFRAME SLIVER
60
50
40

Fig. 6 (*f*)

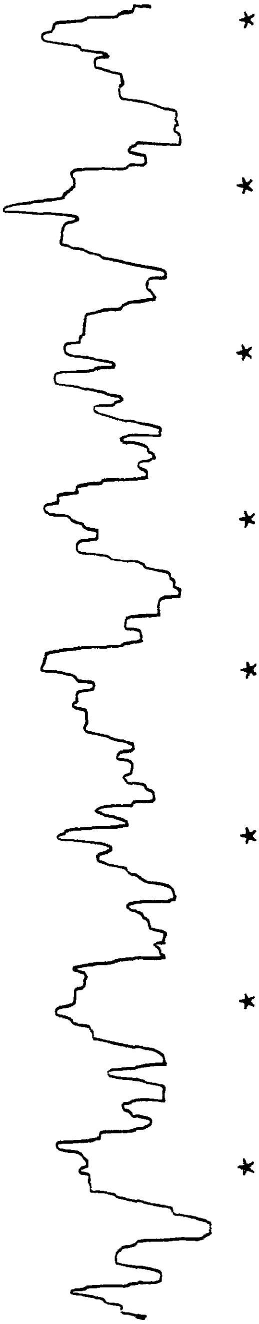

Fig 7. Bent 2nd roller, 0·21 Hk DF9/5/, 4/3/48.

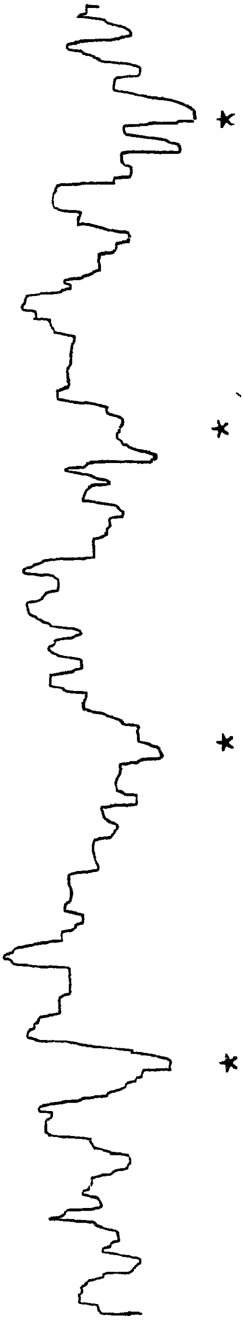

Fig 8. Bent 3rd roller 0·21 Hk, DF2/4, 14/2/48.

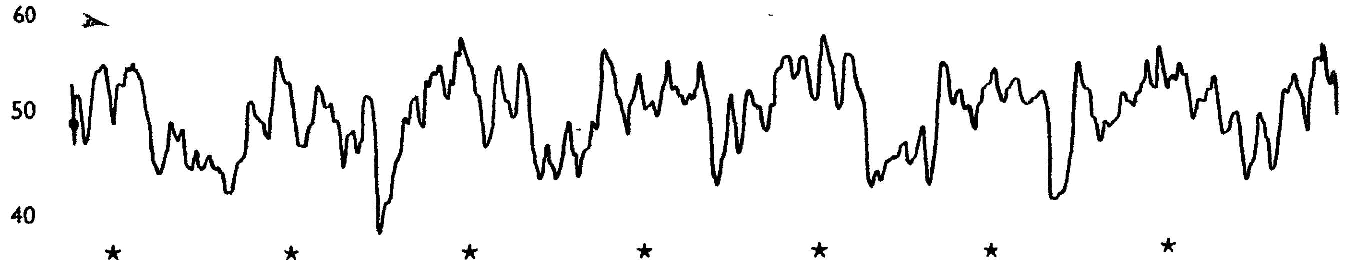

Fig. 9. Eccentrically bored 2nd roller pinion. 0·21 Hk, DF25/1, 16/7/48.

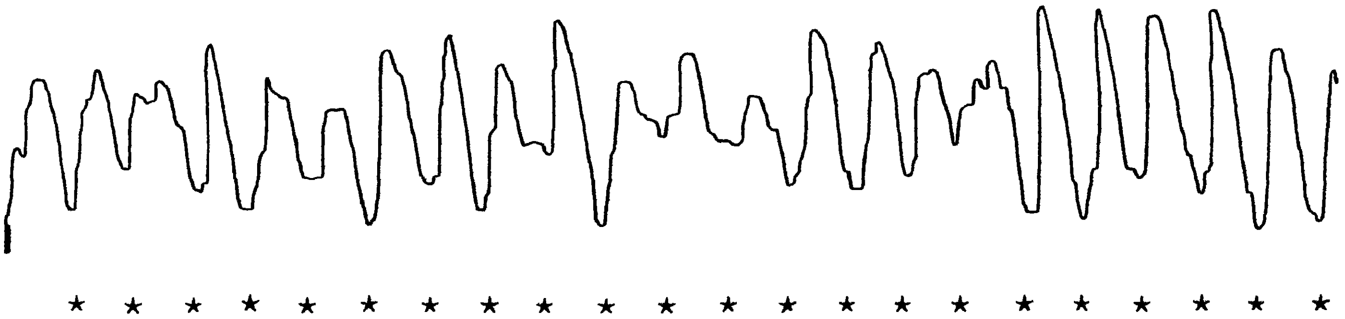

Fig. 10. Worn front top roller. 0·21 Hk, DF5/6, 26/2/48.

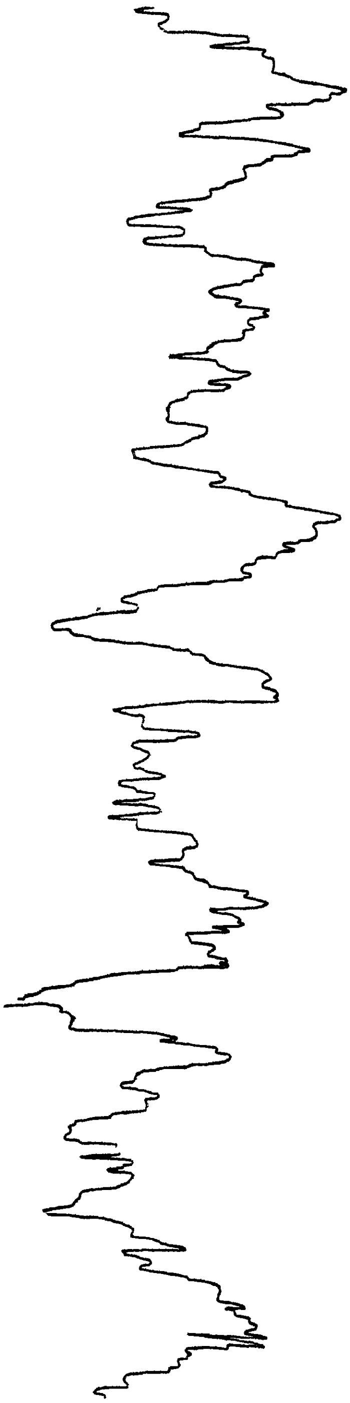

Fig. 11. Broken front roller stand 0 21 Hk, DF24/1, 2/2/48

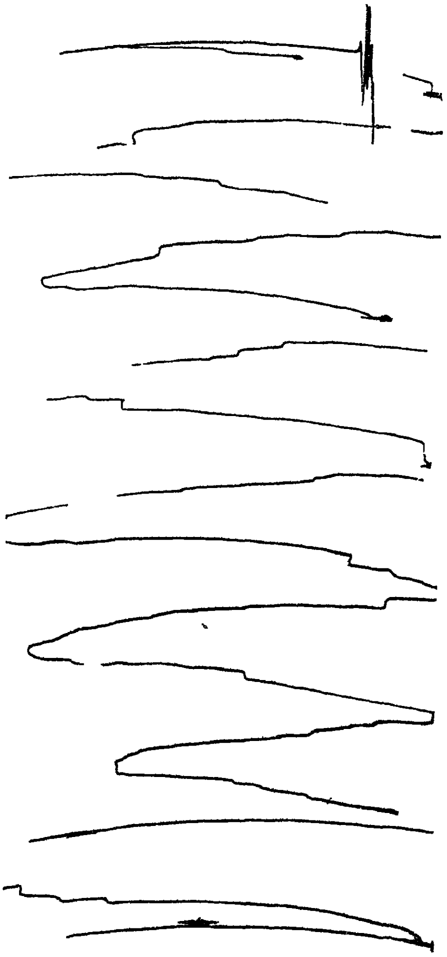

Fig 12. 2nd Roller weights resting on bar. 0.13 Hk, DF13/2, 26/2/48.

16—DOUBLE TWIST SPINDLES.

THE PRINCIPLE OF DOUBLE TWISTING AND A REVIEW OF THE LITERATURE

By G Dakin and E. J. L. Smart

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I. INTRODUCTION

It is generally accepted that the insertion of twist in a thread demands that one end of the thread is held fast and the other end is rotated round it. This principle is embodied in all the long-standing methods commonly used in the textile industries for inserting twist in a thread,* as for example, (*a*) inclined (mule) spindle, (*b*) ring and traveller, (*c*) flyer, (*d*) cap and (*e*) uptwister. Although in trade practice the axis of the thread is caused to depart from a straight line during the twisting process (for convenience of thread control and bobbin formation), yet the conditions obtaining are essentially similar to those when the thread is straight. For each of the conventional devices just referred to, in which the prime mover is a rotating spindle, one turn of twist is inserted in the thread for each revolution of the spindle. It can, however, be readily demonstrated that, although the rotation of one end of a thread relative to the other is sufficient for twist insertion, it is not essential. A thread may be twisted without relative rotation of its ends at all This may be demonstrated with reference to Fig 1. If a short length of tape is held in the form of a loop with both ends fixed and the longer leg is rotated round the shorter so that the same side of the tape always faces the axis of rotation (Fig. 1a) the tape becomes twisted If, after one complete rotation the tape be straightened out (Fig. 1b) it will be found to contain *two* complete turns of twist. This is the basis of "double-twist" or "loop" twisting. The same effect is produced if the longer leg of the loop is translated round the shorter leg, i e if the longer leg of the loop is moved bodily round the shorter leg so that the tape always faces the same direction (towards the reader in Fig. 1c). These methods of twist insertion are not to be confused with other methods of obtaining "double-twist" which make use of two rotating spindles of the conventional type in tandem as illustrated in Fig. 2. In this instance only one twist is inserted in the thread for each revolution of each spindle.

A potential advantage of the "two for one" method of twist insertion will be apparent, since the rate of twist insertion is doubled for a given spindle speed. Commercial applications of this principle exist, and as a matter of interest, it may be stated that the first double-twist spindle traced by the authors was patented 93 years ago In the last year or two, renewed interest has been shown in the matter, following the introduction into this country of a double-twist spindle manufactured by the German firm, Barmer Maschinenfabrik A.-G., and commonly referred to as the "Barmag" spindle.[110] A high speed double-twist spindle designed by Saco-Lowell has also attracted considerable attention.[111]

The aim of the present paper has been to trace the development of the double-twist spindle from its inception by a review of the literature, with special reference to the patents which have been filed, of which a comprehensive list is given This forms the main body of the paper (Section

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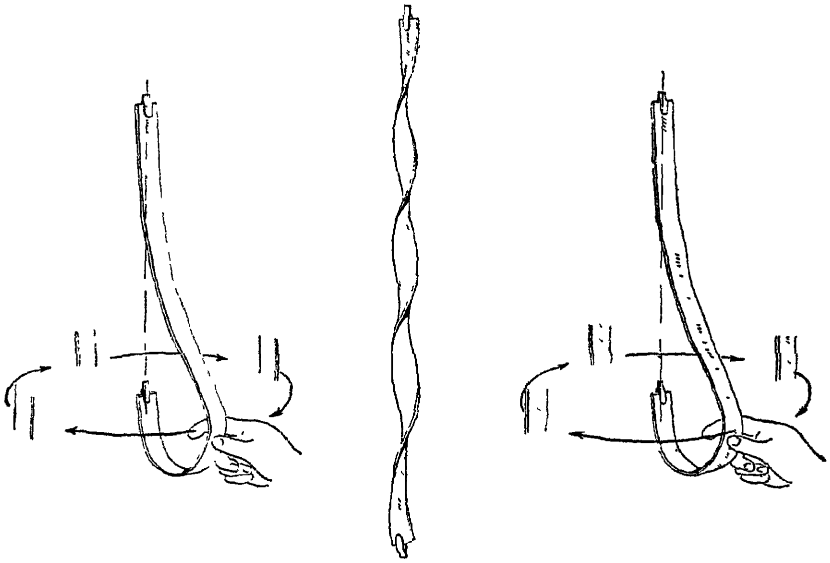
* "Thread" is used here and subsequently in its broadest sense to include sliver, roving, yarn, etc.



(a) (b) (c)

Fig 1

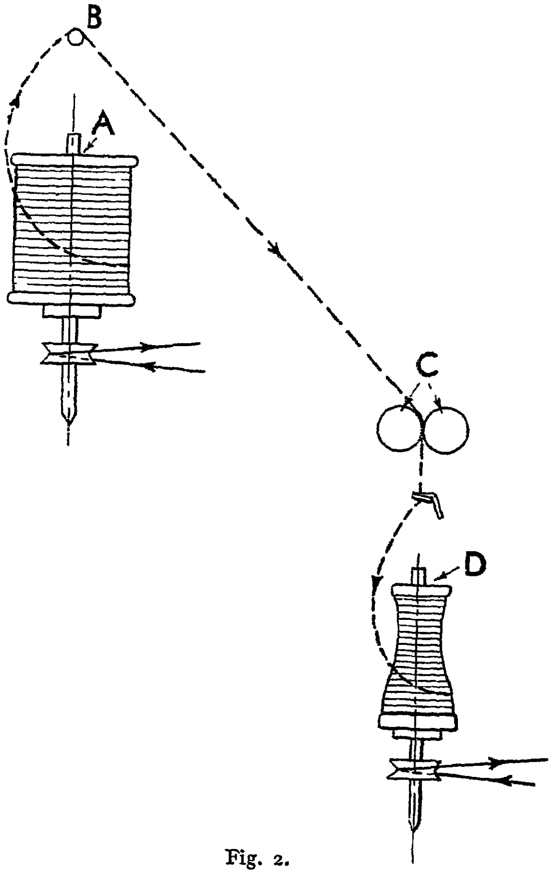


Fig. 2.

III), and it is preceded by Section II which introduces the underlying principles of the double-twist method of twist insertion and considers its application to textile machines

II. THE DOUBLE-TWIST PRINCIPLE AND ITS APPLICATION TO TEXTILE MACHINES

The Double-Twist Principle

In considering the twist inserted in a thread it will be necessary first to consider the definition of twist. The kinematics of twist as applied to textile yarns has been the subject of a paper by Woods;[97] for this reason it is not proposed to enter into more detail than is sufficient for immediate requirements.

Consider a straight uniform cylinder as shown in Fig 3. Let AB be the axis of the cylinder and CD *any* line on the surface parallel to the axis, so that AC and BD are the radii joining the axis to the chosen line. If the cylinder be untwisted as in Fig. 3a the *transverses* AC and BD lie in the plane containing the axis AB and the *generator* CD. If the lower end of the cylinder be rotated with respect to the upper, the cylinder becomes twisted, the generator CD assumes the shape of a helix CD_1 and the transverse BD is displaced to BD_1 (Fig. 3b). The twist in the length AB of the cylinder is defined to be equal to the amount of rotation suffered by the transverse BD, relative to AC, i.e. the angle DBD_1. In general the twist in a cylinder may be defined as the amount of rotation of the transverse to any given generator, per unit length of the axis. We shall make use of this definition when considering threads twisted on the double-twist principle.

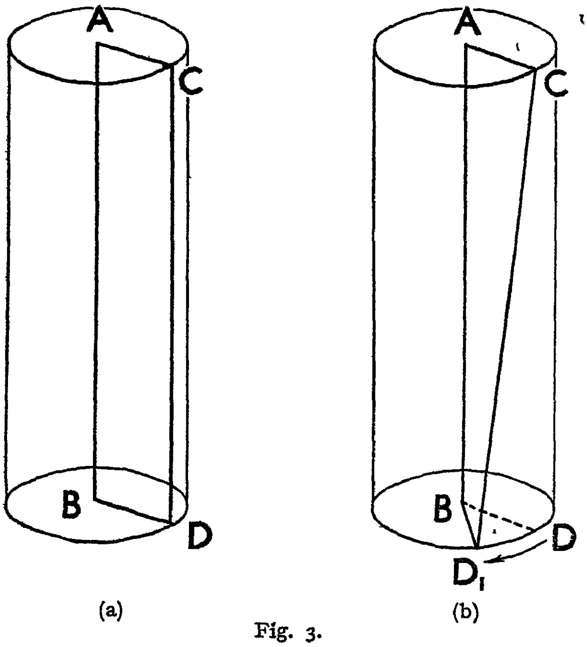


Fig. 3.

The configuration of the thread on the double-twist type of spindle may be as shown in Fig. 4. It will be observed that the thread assumes the form of a loop ABC, of which the axis of rotation is the line AC Both the ends A and C are fixed. In practice the loop is rotated by suitable means, and thread is delivered from the region of C and taken up at the point A, or vice versa, so that the process is continuous, the relative speeds of rotation and withdrawal determining the actual twist inserted per unit length of the thread.

For convenience in considering the twist inserted in the thread for a given rotation of the loop, we shall divide the loop into two sections, one above the line BC and the other below it. The twist inserted in the first section, i.e. in the length AB for a given rotation θ may be considered with reference to Fig. 4 and also to Fig. 5a, which represents a view of Fig. 4 from above. For the initial untwisted position represented by the line OO_1, the transverses BL and AM are coplanar with the generator ML. After a rotation θ clockwise BL assumes the position B_1L_1, AM remaining fixed. The transverse B_1L_1 is then inclined at an angle θ to AM and the generator ML assumes the configuration ML_1. The twist in the length AB of the thread is thus equal to θ, the amount of rotation. It remains to consider the extent of the rotation of BL to a transverse in the thread at C

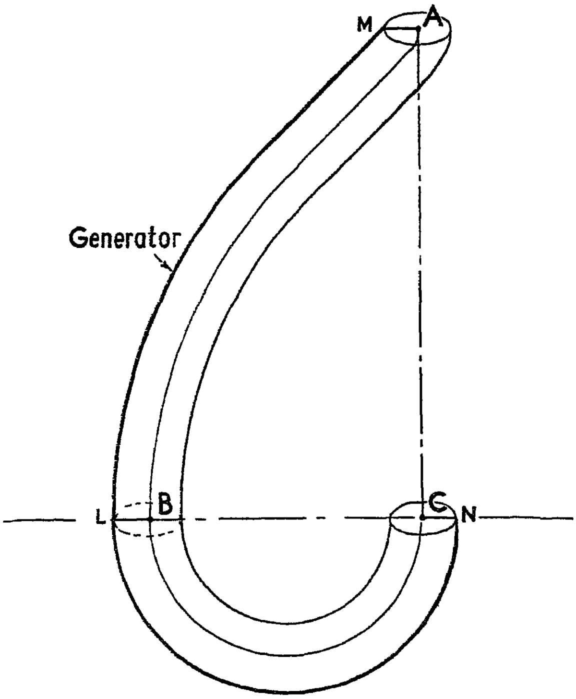


Fig 4

Fig 5b refers to the lower half of the loop As in Fig. 5a BL represents the transverse at B, which is coplanar in this instance with the generator LN (on the underside of the loop BC) and the transverse CN in the thread at the second fixed point C. For a rotation θ it is apparent from Fig. 5b that the twist inserted in the loop BC is again θ, the angle between the transverses CN and B_1L_1. The total twist in the loop ABC is the resultant of the twists in the two portions AB and BC. Since the section at B has been rotated clockwise an amount θ relative to the fixed section A and the rotation of section C is θ, also clockwise, relative to section B, it follows that the total rotation of C relative to A is 2 θ for a given rotation θ of the loop Each complete rotation of the loop therefore inserts two twists in the thread.

The case in which the loop ABC is *translated* round the axis AC may be considered with reference to Fig. 5c. In this instance, since there is no relative rotation between A and B we may consider only the motion of the bottom half BC of the loop, with reference to the transverses BL and CN and the generator LN. For any displacement θ of the loop, transverse CN at C remains fixed and the transverse BL at B assumes the position B_2L_2, parallel to its original direction. With respect to the axial plane through B_2C it is apparent that in the displaced position BL has rotated θ anti-clockwise and CN also θ anti-clockwise. From Fig. 5c it is apparent that these twists are additive and the twist in the loop is again $2\ \theta$. "Double-twist" is therefore obtained when the leg AB of the loop ABC is either rotated or translated round AC, but it should be noted in the above treatment that only the ends and a selected middle point of the loop have been considered *Distribution* of the double-twist between these points is a matter calling for further attention and may, indeed, well defy simple analysis.

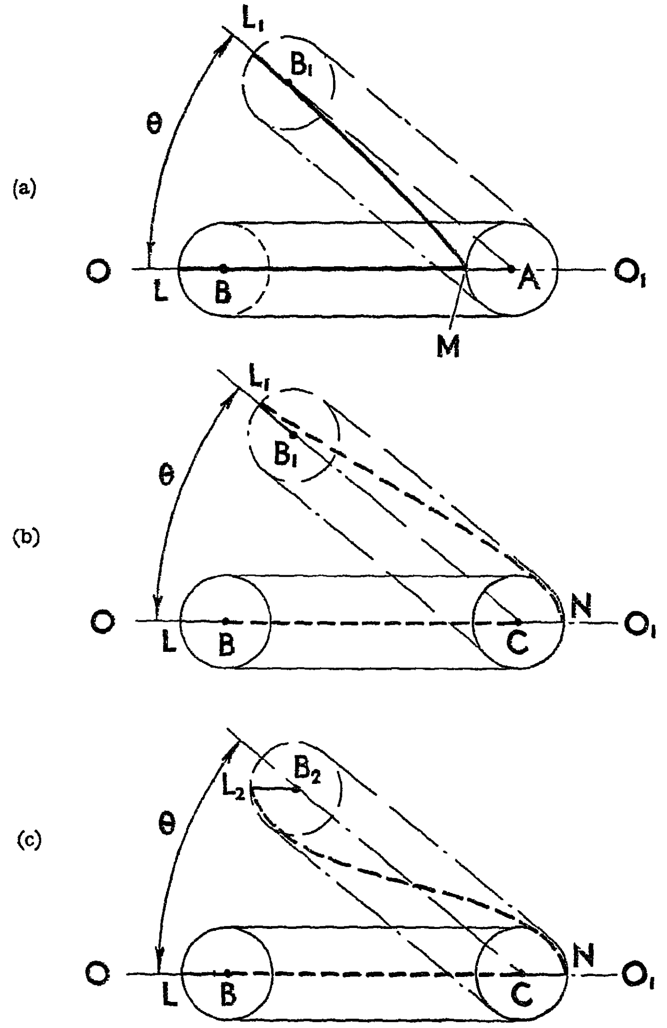


Fig 5.

Application to Textile Machines

In considering the possible commercial application of the double-twist spindle, as with all innovations, many factors have to be taken into account, including capital cost, maintenance and repair, labour requirements, ease of manipulation, production and yarn quality. The only data available on some of these items at the time of writing apply to the Dunlop double-twist spindle (see Appendix), but a brief discussion of some relevant factors referring to double-twist spindles in general may be of interest.

It will be clear from what has gone before that the fundamental condition for double-twist insertion requires one leg of a loop of thread to be rotated or translated round the other leg, both ends of which are prevented from rotating. For commercial use it is of course essential that the twisting process be continuous so that application of the double-twist principle must take into account a *running* thread, the direction of motion of the thread being either from or towards the spindle. This demands a suitable source of supply of the untwisted thread and means for accommodating the twisted thread Control of the package inside the rotating loop raises problems, which above all others are responsible for the diversity in design of the physical embodiment of the double-twist principle The longer leg of the loop is rotated by a spindle and "balloons" round the shorter leg which is either withdrawn from or wound on to a package encircled by the balloon There are two problems, (*a*) to ensure that the motion of the spindle package, if any, is unaffected by the rotation of the spindle itself, and (*b*) to accommodate the largest spindle package possible These will now be considered

Control of Spindle Package.

Owing to the necessity of maintaining a package *inside* the encircling "balloon" of thread formed by the rotation of the outer leg of the loop, there is no alternative to mounting it on the spindle that rotates the loop. In this connection the problem of unwinding yarn *from* a package contained within the balloon is much simpler than that of winding the twisted yarn *onto* a package In the earlier types of double-twist spindles the problem of maintaining the spindle package stationary presented considerable difficulty, mainly due to the fact that suitable bearings of a low friction type were not readily available. Various means were tried for mounting the package carrier so that it was unaffected by the rotation of the spindle, e g. epicyclic gear trains, friction devices, oscillating stop mechanisms, eccentric mounting of the spindle axis, electro and permanent magnets and gravity control. The gravity method appears to have found most favour, probably because of its cheapness and simplicity, but it suffers from the disadvantage that its action is not wholly positive The package carrier is mounted on the rotating spindle by means of ball or roller bearings and any tendency of the carrier to follow the spindle rotation is opposed either by a restoring couple supplied by a weight acting on the package carrier or by the braking action of a suitably mounted weight. This type of package control demands an inclined or horizontal spindle, the angle of inclination must not approach so near the vertical that the weight would prove ineffective in preventing rotation of the package It will be apparent that if the spindle-to-package bearing should "seize" on the gravity control method, an unbalanced system would result which would be set in rapid rotation with consequent danger of bursting

Of the other methods, it would appear that only the magnetic system has survived, this type of control enabling the supply package and spindle to be maintained vertical The employment of gear wheels or friction rollers on the epicyclic principle is perhaps the most obvious method of maintaining the spindle package stationary, and was used by Kirkman[1] as early as 1855 It has the advantage of positive control over the motion of the package within the ballooning thread and allows of the use of a vertical spindle. On the other hand spindle design is complicated and spindle speeds are limited by the additional rotating mechanism involved. The various methods of package control—gravity, gear trains and friction rollers, magnetic and eccentric axes, etc —are described in Section III, and in fact form the basis for classification of the various types of double-twist spindle there dealt with.

Size of Supply Package

The usual alternative types of textile packages—cheese, cone, double-flanged bobbin, etc —can be used on the double-twist spindle, of these the cheese and double-flanged bobbin have found most application. The question of space limitation and the need to utilise the available space to the fullest extent may call for preparation of the spindle package on specially designed winding machinery.[101,106,107] For supply packages using over-end withdrawal of the thread, special auxiliary guiding and tensioning devices are used.

The actual size of spindle package is governed by various conflicting factors and the choice must of necessity be a compromise. A large package necessitates, of course, a large disc or flyer in order that the ballooning thread may clear the package, and this implies a reduction in maximum spindle speed and increase in the gauge of the machine. Spindles with two bearings and flyer arms between them make the greatest use of gauge and frame space, so far as horizontal spindles are concerned (see Fig. 6). It is only required that the flyer should just clear the yarn from the spindle package and the take-up or delivery point can be placed very near to the inner bearing through the axis of which the yarn passes. The use of two bearings and flyer arms, however, complicates the spindle and increases the cost of manufacture. Further, the greater rotating mass involved calls for reduced spindle speeds and is potentially dangerous to the operative

Inclined and vertical double-twist spindles economise in frame width and the type of spindle package employed is not subject to the same limitations as for a horizontal spindle. With one type of inclined spindle[110] the body of a flanged bobbin serves as the supporting medium between the lower twisting portion of the spindle and the upper part through which the yarn is drawn off.

Table I
Comparison of Spindle Package Sizes

	Type of spindle		
	Double twist		Single twist
	Dunlop (Horizontal)	Barmag (Inclined)	Ring (3½″ dia ring, 7″ lift)
Type and size of spindle package	Cheese Dia 4½″ Traverse, 3″	Flanged bobbin Dia, 6¼″ Between flanges, 5⅞″	Taper bobbin Dia, 3″ Lift, 7″
Approximate volume of yarn on full bobbin (cu ins)	45	105	40
Spindle speed (r p m)	3,500	6,000	5,200
Spindle gauge (ins)	9	16½ (two tiers)	5
Approximate frame width	3′2″	2′6″	3′8″

For reasons already given, double-twist spindles will in general be spaced much farther apart than conventional ring spindles twisting similar material On the other hand the inclined and vertical double-twist spindle lends itself to the "double-decker" type of frame construction which offsets to some extent the increased spindle gauge. Further, if a continuous belt is used to drive the spindles, an appreciable reduction in frame width may be obtained so that the floor space required per spindle is further reduced on that account. To give some idea of the differences that obtain in practice, Table I has been prepared showing the sizes of spindle package, speed, gauge and frame width for the ordinary ring spindle and two types of double-twist spindle (Dunlop and Burmag) when twisting 23s/5 tyre cord.

As regards package size, the main interest lies in a comparison of the *spindle* packages, since the size of package external to the spindle is not subject to the same limitations and requires separate consideration It will be observed that the gauge of the Dunlop spindle is nearly twice, and of the Barmag spindle over three times that of the conventional ring spindle. On the other hand the Barmag spindle package is considerably larger than the ring spindle package, but there is little difference between the latter and the Dunlop spindle package. (It may, however, be stated that experimental work is in progress by Messrs. Dunlop Cotton Mills to increase considerably the size of the package for their spindle.) As regards spindle speed it seems safe to assume that the Barmag spindle will run at speeds at least equal to those used on the ring spindle so that the rate of twisting will be doubled. The limitations upon speed imposed by air resistance when using the large balloons necessitated by large supply packages on the Barmag spindle is, however, a matter calling for investigation.

Not until all the relevant factors affecting production have been taken into account is it possible to decide whether the double-twist spindle will show a worth-while advantage over the "single twist" spindle, but enough has probably been said to make it clear that the advantage gained, if any, is not as clear cut as the "two-for-one" twist principle would suggest. (See also Appendix.)

Comparison with Conventional Spindles.

In dealing with the various aspects of design, manipulation, etc., of the double-twist spindle it is convenient or even necessary to draw a comparison with existing types of spindle in common use, so that the advantages and limitations of the very attractive "two-for-one" principle of twisting—which appears very much like something for nothing—may be viewed in their proper perspective. The authors' first-hand experience of double-twist spindles is very limited and in what follows reference is made to such information as is available in the technical press or to claims in patent literature, the source of which is given.

Double-twist spindles have a big advantage over conventional spindles in that neither the delivery nor take-up packages are rotated for the purpose of twist insertion.[90,93] Power requirements are stated to be reduced in consequence [93,100,104] According to one authority[102] the power required per pound of thread twisted on the Dunlop double-twist spindle is less than half that required by the ring doubling spindle. As regards production, increases of 100 to 150 per cent. have been claimed[93] in the twisting of fine yarns, combined with greater regularity of product.

The double-twist spindle itself cannot be considered much, if any, more complicated than the conventional ring spindle, but threading-up of the spindle is more difficult and careful supervision is necessary unless individual stop motions are fitted [101] It is claimed that doffing becomes a more continuous process without the rush periods common to some other types of twisting frames.[89,101,102] Risk of oil-staining is small since there are no rings to be lubricated and the spindle bearing lubricant can be isolated effectively from the neighbourhood of the thread [89,92,102,104]

On the ring doubling spindle, thread tension is dependent on the motion of the traveller and tension variations occur from ring to ring and traveller to traveller.[102] On the other hand a variety of tensioning devices is applicable to double-twist mechanisms ranging from friction pads to positively driven rollers,[105] and with reasonable care tension variations between double-twist spindles of the order of those experienced between ring spindles may easily be avoided.[89] The arrangement does not lend itself to wet doubling,[104] but one attempt at least has been made to overcome this limitation.[82]

Future Developments.

The future development of double-twisting would seem to lie along similar lines to those followed by the more normal twisting methods; that is to say, the birth of the basic idea succeeded by a series of improvements and modifications over a number of years, relating only to secondary details which leave the original principle unchanged.

Possible developments of this type might be expected to include the employment of new alloys and plastic mouldings for lighter discs, flyer and spindle parts which allow of increased spindle speeds, spindle construction more compact in relation to the size of package carried and, in turn, modifications to bobbin and package dimensions and structure, reduction in spindle gauge and floor space required for complete frames, adaptation of the principle for finer counts; improvements in tension devices, stop motions, winding methods, bearings, etc., modification of spindles for the purpose of wet doubling, and also for direct spinning.

Indications already are that more recently designed spindles, when employed for finer doublings, may attain speeds equal to and even in excess of those possible with normal ring spindles or spindles where the package revolves together with the twisting means. One writer[96] foresees in the double-twist principle a keen rival to contemporary ring and silk twisting methods and considers its application to the cotton spinning process is not far distant; another[101] writing in a more critical vein is of the opinion that the principle is only capable of application economically to crêpes, tyre cords and heavy cabled yarns. It is, of course, in this sphere, where high twists and regularity of product are specially sought after, that the "two-for-one" twist principle is particularly attractive.

Where very even twist is required, two separate twisting processes are said to be necessary on ring or flyer doublers, but the double-twist spindle will insert the same amount of twist at one operation to give a product of equally good quality[93] In this connection the action of the double-twist principle is considered to be "kinder" on the yarn because the twists are inserted at different points along its length, and also because of the fact that for an equivalent production rate the spindle speed is halved.[100] A general claim is that of reduced variation in twisting tension and turns per inch[88,100] Absence of snarls on starting and stopping the frame is also often claimed[89,90,92,102,106,108] For these reasons the double-twist spindle has so far found its main application for twisting heavy cords, tyre and rayon crêpe yarns

III. SURVEY OF PATENTS AND LITERATURE

Double Twist Spindles

It is not possible to indicate, even approximately, a date when the principle of loop twisting was first applied to spindle apparatus. The idea is by no means a new one and may even date back to the days when the rapid industrialisation of the cotton industry produced a spate of inventors pressing eagerly forward in the footsteps of the pioneers. The first patent for a double-twist spindle which the authors have traced was taken out by Kirkman in 1855.[1] The construction is elaborate by modern standards and this would seem to suggest that the invention was by no means a first attempt. It was followed by many others from different sources and by 1900 the double-twist principle had been thoroughly exploited. For instance, Golding's[11] patent of 1890 is outstanding for its show of ingenuity and diversity of application. The specification, which is extremely lengthy and contains over sixty plates, describes arrangements for inserting four or more turns at one operation, or for carrying two packages, each thread being separately double-twisted. The inventor thoroughly explored means for retaining the package stationary, including eccentric mounting of the spindle axes, magnetic and gravity controls The patent also covers arrangements for winding onto or drawing off from the package, rollers and roller heads; thread guides; spindle lubrication; independent braking; building motions and stop motions.

It would be interesting to know why these early inventions never attained practical application in the trade. Perhaps the difficulty of retaining the package stationary was not satisfactorily overcome, for there are accounts of double-twist spindles being dangerous and "exploding"; or perhaps the inventors lacked the necessary backing to carry their ideas beyond the embryo stage. Whatever the reason may have been there is, it seems, only one recorded instance of the application of the principle to an actual machine. This was a frame constructed in Manchester by Shepherd and Ayrton (now Wm. Ayrton & Co Ltd.) in 1887, but there is no record of such frames being employed on an industrial scale.

This survey does not attempt to give full account of the chronological development of double-twist spindles Rather, in order to give the subject matter greater cohesion, patents with similar features are grouped and reviewed in turn, together with brief descriptions of the more interesting and relevant types

All double-twist mechanisms, of whatever type, must conform to two fundamental principles First, the yarn must be looped so that one leg of the loop is translated or rotated round the other; secondly, a package must be mounted and held stationary within this loop. The spindles have been classified according to the method employed for maintaining the package stationary. These are: Gravity Control, Gear Trains and Friction Rollers, Magnetic Means, Eccentric Axes, etc

Gravity Control

The weighted creel or gravity control was employed by King[6,9] in 1880 and 1885, and it seems probable that he was the pioneer of this method.

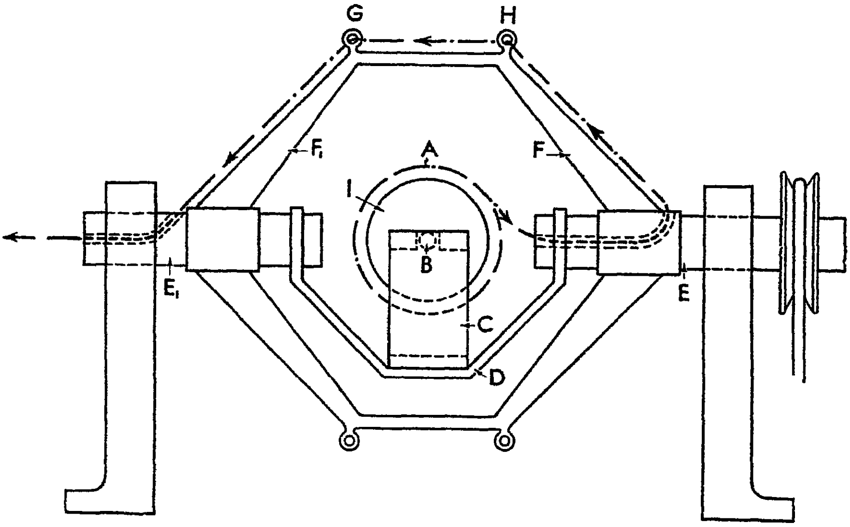


Fig. 6.

(King, 1880)

The spindle (Fig. 6) is of the two-bearing, horizontal type. The yarn is drawn off sideways from the bobbin A which rotates on spindle B supported by vertical arms C of the yoke or cradle D, which is "loosely hung on the hollow revolving spindles EE_1 . . . the centre of gravity of the suspended part being below the spindle axis to avoid rotation". The spindles EE_1 which rotate in the bearings are connected by balancing arms FF_1 provided with yarn guides G and H, and a drag pad I is applied to the rotating bobbin in order to tension the thread King's second spindle,[9] although substantially the same as the first, differs from it in that the bobbin is placed coaxially with the spindles, thus allowing a larger package to be housed in the frame

The main form of King's early inventions has been adopted by many subsequent designers of double-twist spindles of the horizontal type. J. Beck's patent[12] 1898 comprises a very complicated arrangement with drives at each end and a mechanism for winding the yarn onto the bobbin; a similar spindle patented by Fahr[13] 1903 has two horizontal flyers driven for the first time by separate synchronous A.C. motors. Among more contemporary inventions, a spindle patented by Langstreth and Townson,[77] of Dunlop Cotton Mills Ltd., in 1937, still resembles in essence the early spindles of King, with two bearings and a flyer to allow a larger package to be accommodated.

Shepherd and Ayrton's[10] spindle patented in 1886 is of interest because of its departure from the conventional flyer construction which typifies the earlier double-twist spindles The spindle (Fig. 7) is mounted in a nearly horizontal position and the yarn is drawn off over the edge A through the hollow spindle B. For the first time a disc C is employed to clear the ballooning yarn from the bobbin and weighted cradle frame D Provision is made to prevent the escape of lubricant by means of a recessed cup E. This patent certainly marks a step forward in the evolution of double-twist spindles, and as already mentioned, a frame incorporating the spindle was built in 1887. Similar in type to Shepherd and Ayrton's design is the first spindle patented by Andrew and Langstreth[24] in 1926, followed by another patent[25] in 1927. These two spindles were the forerunners of the now well known Dunlop Disc Doubler,[35,87,89,92,102,106,107,108] specially developed for making tyre cords. For this spindle (Fig. 8) which is horizontal, the package A is carried on the weighted bobbin support B, which in turn is mounted on ball-bearings C on spindle D driven by pulley E Disc F serves to clear the yarn balloon from the package as also does ring G. The bobbin A is carried on a frictional washer H fixed to platform I which, to quote the patent specification, is "flotably" mounted on support B and retained by peg J. Several interesting methods of obtaining an even tension from full to empty package are described in the patent specification, including special methods of winding the supply package, dropping water into a receptacle to compensate for the decreasing weight of the package as the yarn is drawn off, and a collapsible drag washer. Similar in design to the Disc Doubler is a spindle patented by Ferier,[38] but in which provision is made for winding the yarn *on* to the spindle package. This is accomplished by means of a gear train driving the bobbin from the rotating spindle and a variable gear to give

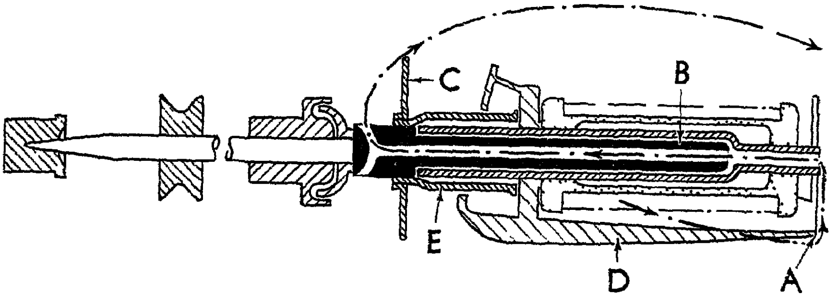


Fig 7.
(Shepherd and Ayrton, 1886)

the necessary range of winding speeds; the whole is housed within the frame of the bobbin carrier, tending to make the spindle bulky and elaborate, thus affecting adversely the cost of manufacture and ease of operation.

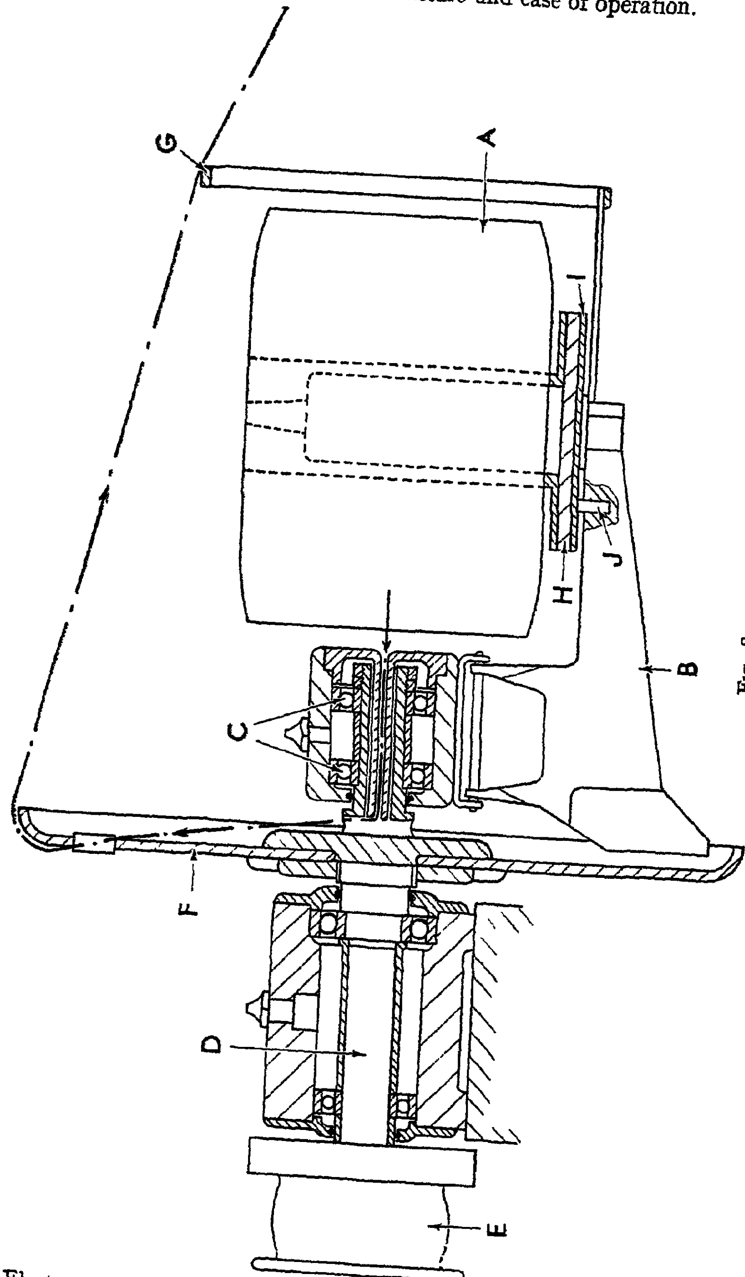


Fig 8
(Dunlop Cotton Mills, Andrew and Langstreth, 1929)

Electric drive for individual spindles is the feature of an invention by Baudonnel and Berthier[26] in 1927. A further invention[34] in 1929 incorporates for the first time an electric stop motion which operates if the bobbin carrier turns or the thread tension becomes too high The spindle itself is rather elaborate and this coupled with the use of stop motions would make the cost of manufacture very much higher than that of a normal ring doubling spindle. Electric stop motions of the same type are also the feature of spindles patented by the Soc. Textile Twistok[64,65] of France These stop motions operate when the supply package approaches exhaustion, any single yarn breaks, the tension of the combined yarns becomes excessive, or the bobbin carrier is displaced. The system is operated by feeler contacts which close the circuit of an electro-magnet connected to the main motor switch or main drive so as to disconnect the drive on completion of the circuit. Connection between the feeler contact circuits within the flyer and the outside source of current is achieved by means of brushes and slip rings fixed to the rotating spindle shaft next to the driving pulley An interesting arrangement of horizontal dual bearing spindles in units of three is known commercially under the name "Comatex" This frame, an invention of the Comptoir de Matériel Textile[76] in 1937, consists of units of three spindles mounted in banks. Each spindle has two discs, not joined as usual by flyer arms, but synchronised by a chain drive from a common driving shaft, this arrangement ensuring uniform insertion of twist. The spindles are also provided with positively driven drawing-off rollers situated on the package carrier at the entry of the twisting axes. The machine is evidently designed for heavy cabled yarns since the separately twisted threads from a unit of three spindles are passed to a delivery roller and then grouped for winding on the take-up bobbin; this bobbin is then placed in a similar machine and again cabled Considerable attention has been paid in the design of this machine to the maintenance of even tension and delivery speed, and the makers claim a high degree of twist regularity. The patent specification states that electric stop-motions of the type described in the patents of Baudonnel and Berthier[34] and of the Soc. Textile Twistok[64,65] may be fitted.

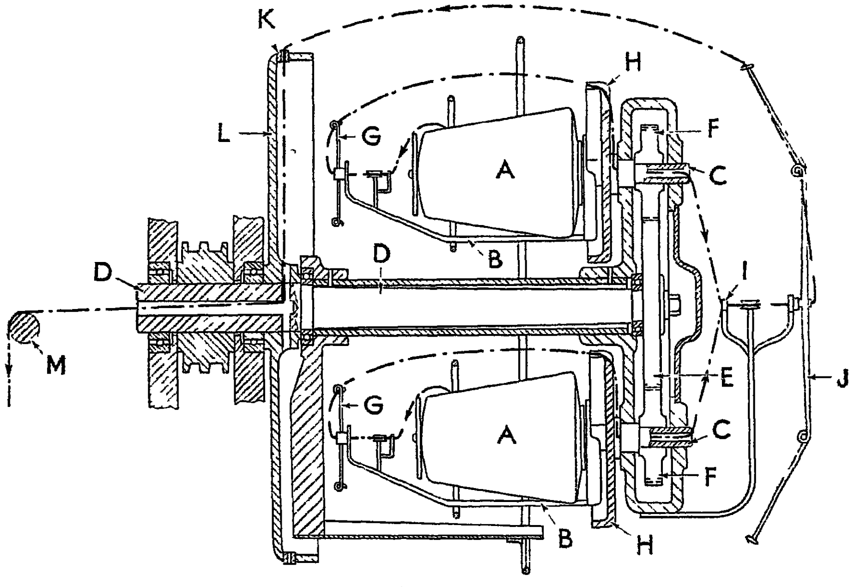


Fig 9.
(Soc Italiana Pirelli, 1933)

Also in the field of heavy cords, a spindle developed by Soc. Italiana Pirelli[63] (the tyre firm) is of interest. This arrangement comprises in effect a multiple double-twist spindle, for within the main spindle assembly two or more subsidiary spindles are mounted. In Fig. 9 only two packages A are shown and these are held stationary in carriers B slung loosely on the axes of spindles C. The whole is mounted on the main rotary spindle D, which drives spindles C by gears E, F. The yarn drawn off packages A passes through freely mounted flyers G, through guides on discs H and hollow spindles C to a doubling eye I and freely mounted flyer J, then through guide K on disc L and rotary spindle D to delivery roller M. Thus the separate yarns from the packages A are first given a double-twist and then combined by a final double-twisting Whether this elaborate spindle has ever been employed in production is not known, but in common with all such complicated devices it is probable that the spindle speeds will be relatively low and that operation and maintenance may be too involved for practical purposes.

Up to this point horizontal spindles alone have been dealt with; this type is usually bulky and requires considerable space when mounted, resulting in a rather large frame width. In 1907 a spindle was patented by Bebié[16] with the axis *inclined* sufficiently near to the vertical to reduce very appreciably the over-all width occupied by the spindle, without rendering ineffective the gravity control. This invention marked the advent of the inclined spindle, for although some time elapsed before other spindles of this type appeared, within recent years the arrangement has met with considerable popularity among designers of double-twist spindles. Bebié's patent also incorporates a mechanical stop motion in the shape of a pivoted arm which falls to engage with a stop if the package carrier turns beyond certain limits.

Outstanding among spindles with inclined axes is the Barmag (German) spindle, a product of the Barmer Maschinenfabrik A.-G. of Lennep, Rheinland, a firm of textile machinists who have devoted considerable attention to the problems of double-twisting over a number of years. Some indication of their work in this field is given by the number of patents[39,41,42,44,45,50-58,61,67,69,75,79,110] filed between the years 1930-38. As early as 1931, a patent[45] was taken out describing a double-sided twisting frame with inclined double-twist spindles. The "storing ring"[41,42,52] is an interesting and unusual device to compensate for tension variations in the running thread. Some patents[44,50,51,57,71] relate to modifications of driving whorl and disc and of the guiding element which protects the package from the ballooning thread; others[53,56,67] relate to adaptations of the package carrier for different types of packages and numbers of packages and changes in the package control weight,[54,55,58] The spindles are mounted in two tiers on each side of the frame[61] and are driven by an endless belt.[72] In addition, there are contrivances for thread clearing,[69] yarn guiding,[70,72] thread engaging,[79] and sizing or wetting the yarn.[82] A spindle (Fig. 10) developed specially for crêping purposes, has a light wire flyer C, which is rotated slowly by the yarn unwinding from the package. The yarn passes from the bobbin A through an eye in the flyer C, down the axis of the spindle, emerges through a slot D in the storing ring G and doubles back over the guide dome or disc H to the take-up point The yarn package A comprises a double-flanged bobbin fitting on the bobbin carrier E which is prevented from rotating with the spindle by counterpoise weight B The weight B is not fixed rigidly to the bobbin carrier E, but is mounted on a flat ring (concentric with the stub of E) so that although direct rotation of the bobbin with the spindle is prevented by the restoring couple due to the weight B, yet the bobbin carrier E is free to turn slowly during twisting because of the flexible coupling. Uneven wear of the bearing I is thus avoided. Further, this arrangement would appear to assist in damping oscillations of the bobbin carrier and reducing the risk of "bursting" should bearing I seize.

The barrel of the bobbin itself forms the support for the stationary "nose" of the spindle on which flyer C rotates. The spindle is inclined at 25°-30° to the vertical, and is driven by whorl F which carries at its upper end the storing ring G. This device consists of a grooved ring, coaxial with the spindle and located at the base of the guide disc H. The ring carries on its circumference and across the groove a number of short bars and the yarn emerging from the axis of the spindle passes along a radial slot in the ring. It is claimed that any variations in tension as the yarn is withdrawn from the spindle package are compensated for by the wrapping or unwrapping of the yarn on the storing ring. Immediately below the storing ring inclined slots are cut to facilitate threading.[75] Three sizes of spindle have actually been examined by the authors, mounting bobbins of the following dimensions:

	No. 1.	No. 2.	No. 3.
Flange diameter (inches)	3½	6¼	8½
Between flanges (inches)	4⅝	5⅞	5⅞

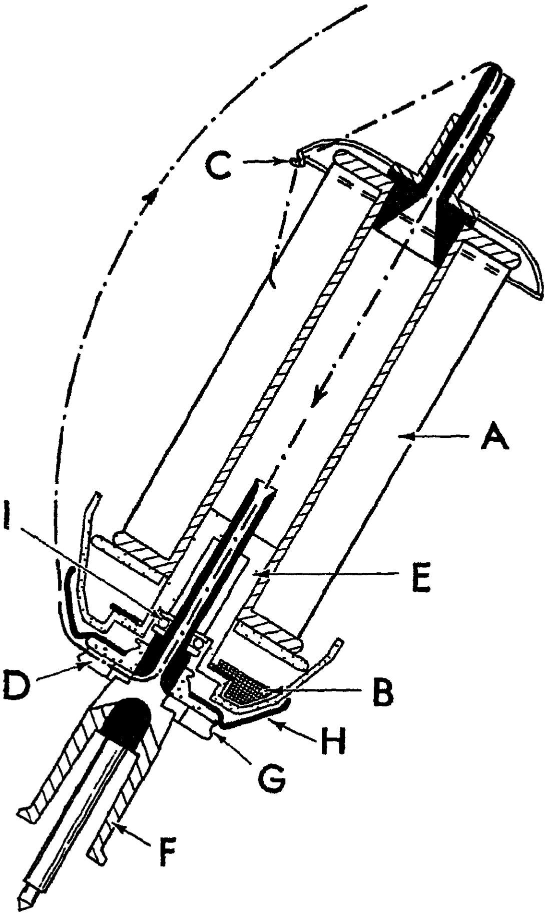


Fig 10.
("Barmag" spindle)

The packages for sizes No. 2 and No. 3 are larger than those hitherto used with double-twist spindles, and it is to be noted that the increase in package size has been obtained chiefly by increase in diameter, rather than length. From such information as is available the development of these spindles has progressed beyond the experimental stage, and it is further understood that experiments on spindle type No. 1 have reached a stage where its application to a full scale frame should not be long delayed.

In America attention has also been devoted to the development of double-twisting, and two patents[78,85] due to Kent cover inclined spindles with individual electric drives, and in which the package is entirely enclosed. A spindle of double-twist construction, for folding together a number of yarns, is the subject of a patent[80] granted to the United States Rubber Co. in 1945.

Control of Package by Gear Trains and Friction Rollers

Three forms of mechanical coupling are usually adopted—gear wheels, friction rollers and pulleys—but the action of all three is similar and only gear wheels will be considered. A stationary gear wheel A (Fig. 11) concentric with the axis of the spindle G and located below the path of the yarn, engages with the lower wheel of the compound gear C, carried by an extended arm of spindle G, located diametrically opposite to the point where the yarn emerges. The upper gear of C engages wheel D which is concentric with the spindle and integral with the bobbin carrier E. The system thus forms an epicyclic train and the package is maintained stationary since no motion is imparted to D by the rolling action of C round it. The yarn passes through the hollow spindle G and over disc or flyer K as shown in the diagram by the broken line.

The principle used for maintaining the spindle package stationary may be illustrated with reference to Fig 11 which does not, however, represent any specific spindle.

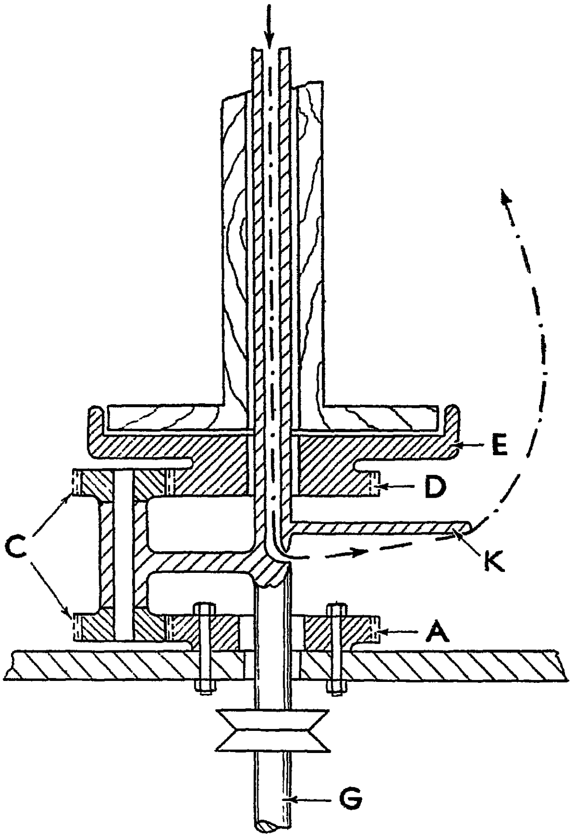


Fig. 11.
(Illustrating use of gear wheels etc. to maintain the spindle package stationary)

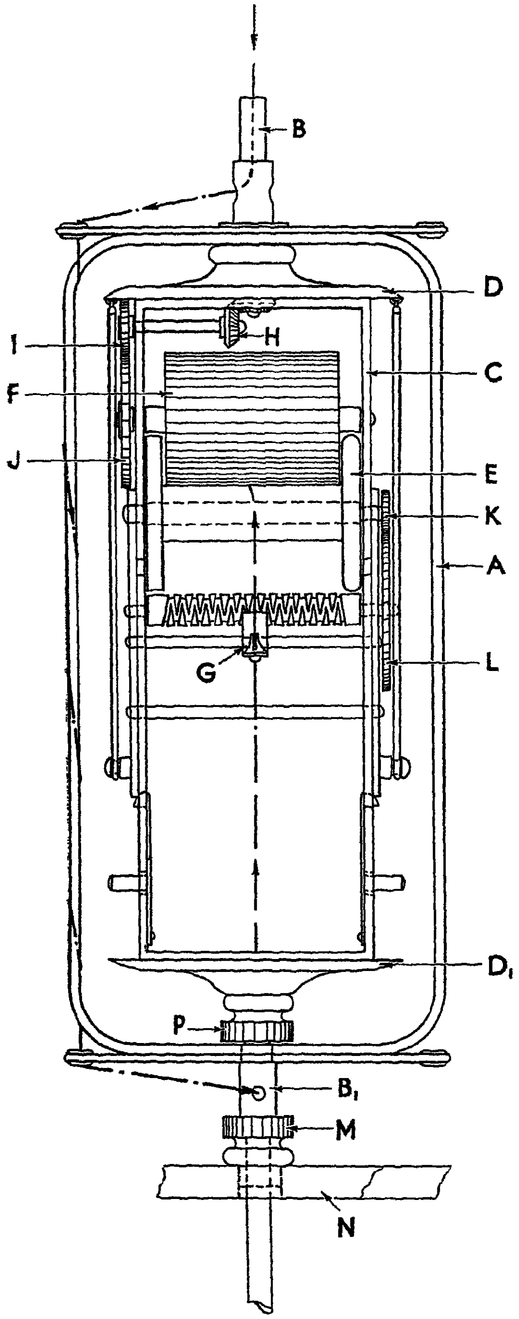


Fig. 12.
(Kirkman, 1855)

Kirkman's spindle (Fig 12), which is of the winding-on type, consists of a vertical flyer A mounted on hollow spindles B,B_1. Within the flyer A and supported freely on spindles B,B_1 is a rectangular frame C terminating in upper and lower discs D,D_1. The bobbin E, its presser roller F and traversing guide G are mounted on frame C. Roller F is operated by gears H,I,J, from the upper spindle B, and guide G is driven from bobbin E by gears K,L. In order to hold frame C stationary, toothed gears are employed, the rotating member (not shown) turning with the flyer A and engaging with wheel M held fast in frame piece N, and with wheel P fixed to lower disc D_1 of frame C. The action of the gears is exactly similar to that illustrated by Fig 11. The yarn is delivered from rollers, enters the hollow spindle B from which it emerges and after being wrapped round the flyer leg enters lower spindle B_1 and thence to the bobbin through traversing guide G. Twist is inserted between the delivery rollers and B, and between B_1 and bobbin E.

Kirkman claims for his spindle, to quote the words of the patent specification: "By this new plan I obtain a much more regular strain upon the roving or yarn, and make it more even and regular in appearance, and in every way a better article, and the flyer is much more simple and inexpensive in its construction than those heretofore used in similar objects." The latter part of this statement would seem further to support the belief that the double-twist principle may already have been exploited before 1855.

The use of bevels to maintain the package stationary is the feature of Clegg and Taylor's[7] invention of 1881, but the arrangement is complicated and the description from the abridged patent specification is very involved. In 1861 a horizontal spindle patented by Dunn[2] incorporates friction rollers to ensure that the motion of the winding-on bobbin is unaffected by the rotation of the flyer, the bobbin itself being driven by friction discs so as to wind on the twisted yarn at a controlled rate, a double-threaded screw being used as traverse. Another horizontal spindle patented by the Société d'Applications d'Electricité et de Méchanique[32,33,91] employs an unusual arrangement for maintaining the spindle package cradle stationary. A large gear wheel fixed to the package cradle engages with a small wheel rotating freely on the horizontal arm of the flyer as bearing, this wheel engaging in turn with a large annular crown wheel, external to the flyer which rotates the small wheel at a speed twice that of the flyer. The speed at which the small wheel on the flyer arm rotates must preclude anything but relatively moderate spindle speeds.

Masson[27] patented a spindle in 1927 which although ingenious in design is mechanically so involved that it is difficult to envisage its application to practical twisting. The yarn path follows the conventional loop through the spindle, and in addition the package is revolved in the opposite direction to the rotation of the loop "further to augment the twist". The rotation of the package is effected by means of pulleys and bands, the creel being held stationary by the same medium. The spindle dimensions must be several times greater than those of the package carried; for driving the spindle and guiding the yarn there are no less than sixteen pulleys; and threading the spindle would amount almost to a major operation.

A neat arrangement of friction wheels and races for maintaining the bobbin carrier stationary is that adopted by Pool of Messrs. British Celanese[47] The spindle is vertical (Fig. 13) and an annular race A provided on the package support B is engaged by one friction wheel C of a pair on a pin D rotating with the driven spindle E, the other friction wheel F engaging with another race G. If the wheels C,F are of the same diameter and the race G is held stationary the package carrier is prevented from rotating. The friction wheels C,F are freely mounted on pin D so that contact of wheels and races is ensured by the action of centrifugal force. Variations in degree of twist may be effected by varying the relative sizes of the friction wheels and races or by rotating the race G, this in effect causing the bobbin to rotate. A guide disc H for the yarn is mounted on ball-bearings on a tube I secured by springs J in the bore of the bobbin. British Celanese Ltd. also hold patents[48,49,59,60,68] embodying the double-twist principle for other types of spindles, tensioning devices and methods of fancy doubling.

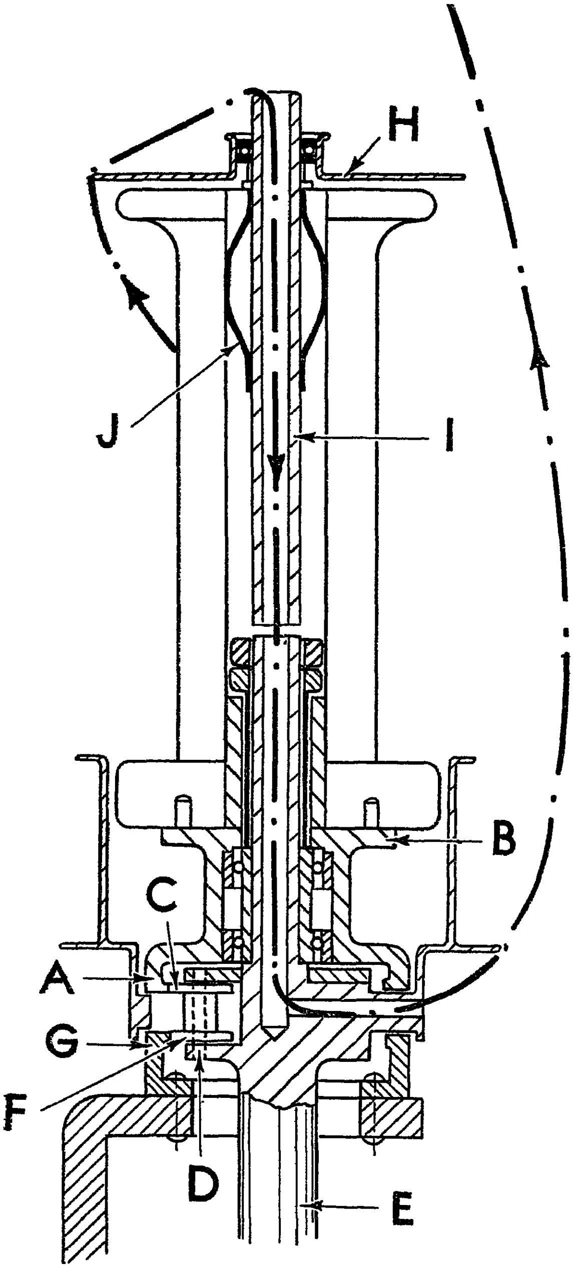


Fig. 13.
(British Celanese Ltd, and W. Pool, 1930)

A recent development[112] which combines the double-twist principle with *rotation* of the spindle package is a feature of a patent[86] by the French firm Rhodiaceta. One such spindle incorporates the normal type of epicyclic gear-train already described, but by choosing a suitable value for the gear-train, the package is rotated in the opposite direction to that of the spindle proper. The "single" twist thus obtained is added to the "double" twist and its amount depends on the speed at which the package is rotated.

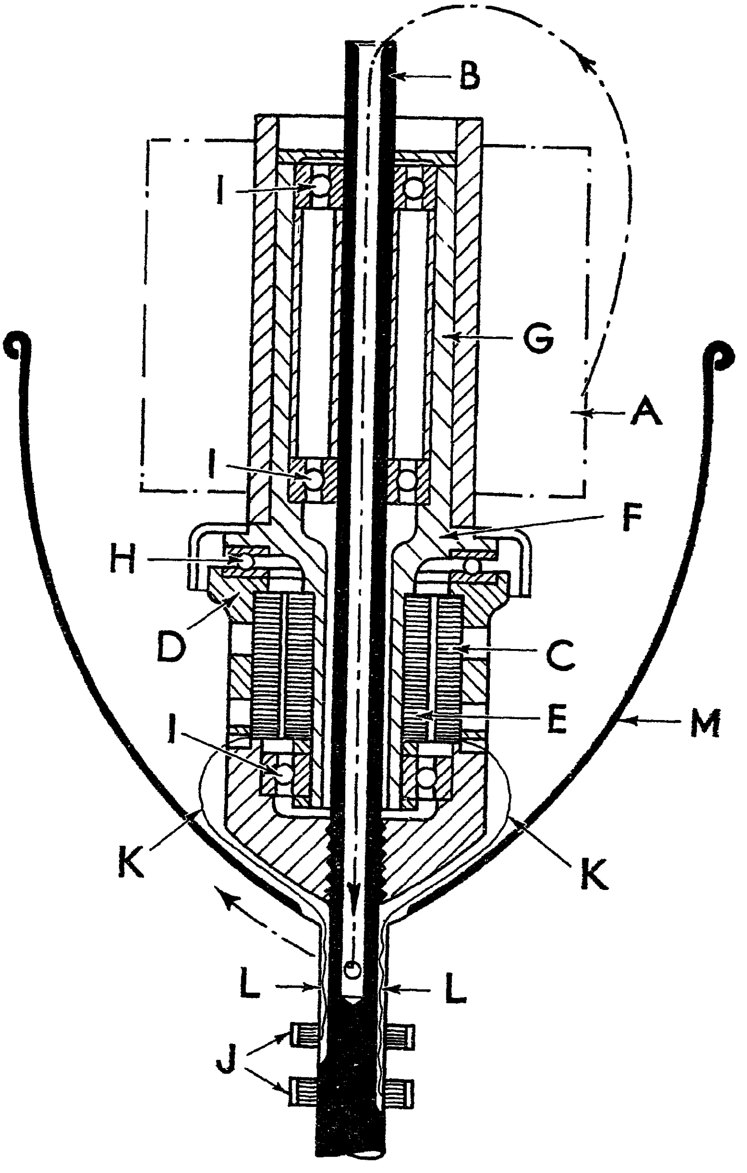


Fig. 14.
(Rhodiaceta, 1946)

The same firm has also developed a spindle which is an interesting elaboration of this principle, the spindle package being rotated by an electric motor, and the spindle itself by the usual pulley or an additional motor. In this arrangement (Fig. 14) the "stator" C of the package-driving motor is mounted on the member D which is attached to the hollow double-twist spindle B just above the base of the spindle cup M The "rotor" E is mounted on an extension of the mandrel F the upper part G of which carries the package A. The weight of the package is supported by the thrust race H, and both mandrel F and rotor E are centred on the spindle B, by ball races I. Slip-rings J, insulated from the spindle but turning with it, feed current to the stator C via wires K lodged in grooves L. The cup shaped guide-cover M prevents the ballooning yarn from fouling the package A. The motor speed must be such that when the spindle is rotating the package A turns in the opposite direction. In effect, the speed of the *rotor* relative to the stator must always be in excess of the spindle speed, if additional twist is to be obtained, the amount of this twist being proportional to the speed difference. For example, if the spindle speed is 5,000 r.p.m. clockwise and the package speed 5,000 r.p.m. anti-clockwise, the speed of the rotor relative to the stator is 10,000 r p.m. and the total rate of twist insertion 2 × 5,000 for the spindle plus 5,000 for the package, making 15,000 turns per minute in all. The same twisting rate could of course be attained by a normal double-twist spindle running at 7,500 r p.m. with the package stationary. No information is given of spindle speeds or performance,[112] but it seems probable that the advantages of this system are not so great as would appear at first sight For a reasonable gain in twisting rate the rotor to stator speed (that is the absolute motor speed) must be very high for a normal range of spindle speeds. Thus, for a gain in twisting rate of one-third the motor speed must be twice the spindle speed. Further, the most suitable motor for this purpose is of the type in which speed is directly proportional to the frequency of the supply current, and as the normal mains frequency of 50 cycles per sec. would give a motor speed of only 3,000 r.p.m., some variable form of frequency conversion would be necessary if impracticably low spindle speeds are to be avoided and the spindle and package speeds varied. The high motor speeds necessary would imply a source of danger if by accident the drive to the spindle were cut, for unless the motor circuit was automatically broken, the package might accelerate to a dangerous level.

Magnetic Control

In their search for a method of package control compatible with the demands of practical operation a few inventors of double-twist spindles have turned to the use of magnetic force. There are in fact only three or four instances from the records available of this method being used, and it is not known to what extent this type of spindle has so far been applied to twisting on an industrial scale.[111]

Magnetic control was applied as early as 1890, and Golding's[11] comprehensive patent of this date specifies the use of permanent and electro-magnets for this purpose. In 1927 two patents are recorded by Durand[29,31] for spindles controlled by a bar and magnet, and a description is given[93] of a frame in which spindles of this type are mounted on both sides in two tiers and are driven by a continuous belt For a frame of one hundred spindles the dimensions specified are, length 17 ft. 3 in., height 4 ft. 5 in , and the width only 17½ in. Each spindle has an automatic stop-motion which operates if the creel tends to rotate or the yarn breaks Durand's spindle is shown in Fig. 15. The bar A of magnetic material is mounted as shown in relation to the magnet B and its spherical ends are centred at point of oscillation C of bobbin D so that the air gap between the bar and the magnet is unaffected by oscillation of the bobbin. The bobbin D is carried by tube E on the end of rotary flyer tube F, on a spherical bearing Flyer G is preferably made of insulating material such as vulcanised fibre. If for any reason the bobbin and bar rotate, the magnet B is released and in dropping applies brake H to driving pulley I, at the same time releasing the tension on the driving band and stopping the take-up rollers. To ensure more positive operation of the magnet when released the bar J is of magnetic material

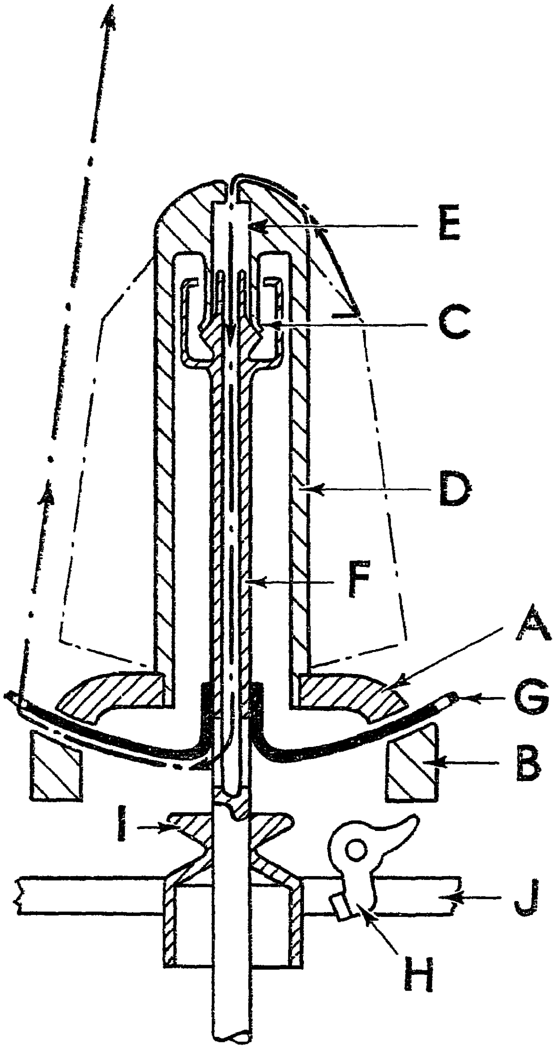


Fig 15.
(Durand, 1927)

Magnetic means with damping coils is the method specified to hold the package stationary in a spindle patented by the Atwood Machine Co.[83] of the U S A. No information is forthcoming as to whether this spindle has been developed further since 1940, the date of the patent, but the Saco-Lowell Shops, also of America, patented a spindle with magnetic control in 1943,[81] and considerable development is in progress, the latest version incorporates individual electric motor drive for each spindle and attains spindle speeds of 12,000 r p.m ,[111] the magnetic arrangement breaking the motor circuit if the package carrier turns This spindle is illustrated in Fig 16 The package carrier A is mounted on the ball bearings B and is prevented from rotating by the action of two diametrically opposed "alnico"

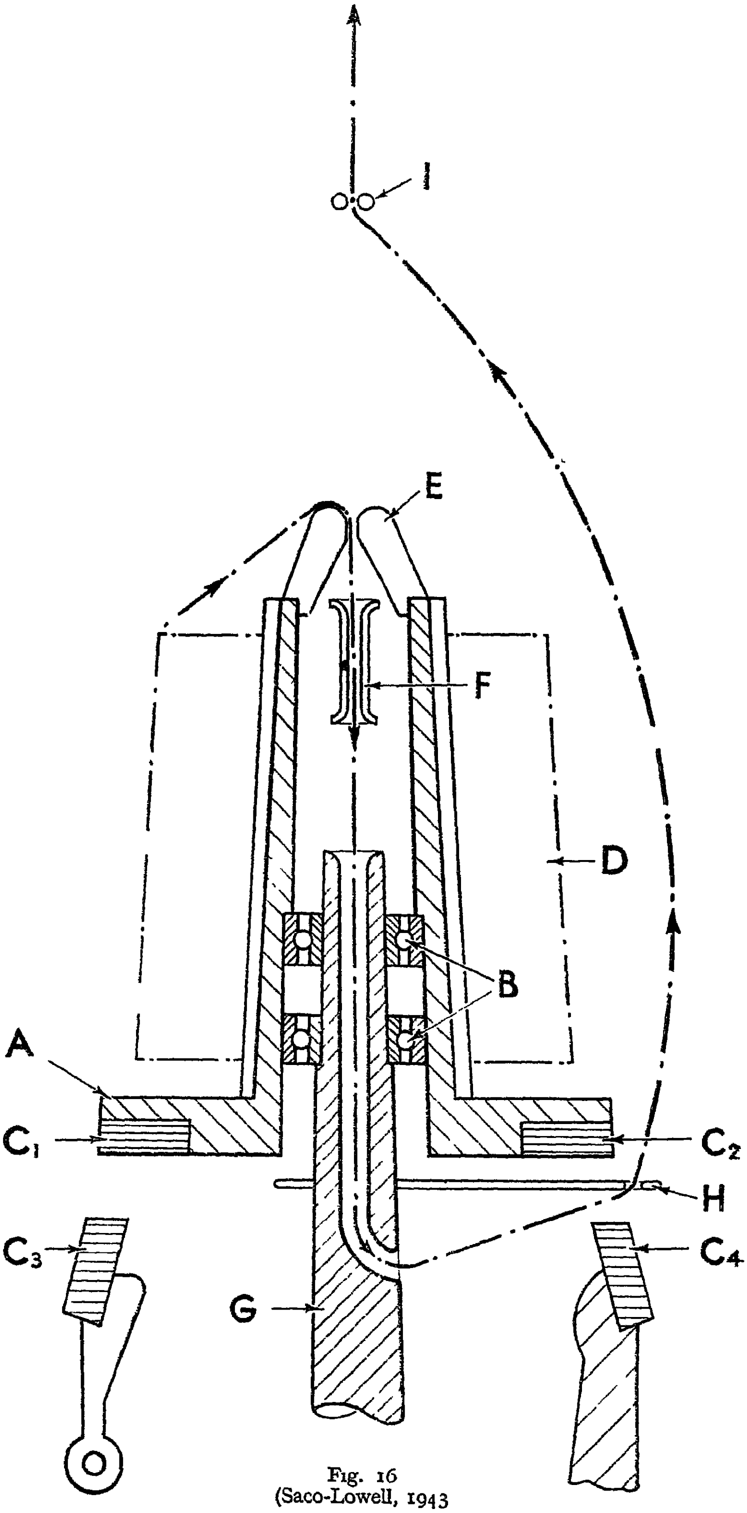


Fig. 16
(Saco-Lowell, 1943

magnets C1,C2 in the base of A, and two similar magnets C3,C4 mounted on the spindle support Magnet C3 is pivoted on a gravity controlled "trap door" arrangement; if carrier A turns by as much as 5° like poles of the magnets become opposed and magnet C3 is repelled, causing a spring loaded brake to operate on the spindle and simultaneously the drive to the spindle is stopped. The yarn is drawn off from the package D, passes through nose piece E and tension device F down the hollow spindle G and emerges sideways to pass upwards through flyer arm H to guide I. The tension device F which is used for rayon yarns, consists of two flat plates pressed together by an adjustable spring Spindle G is comparatively short and is made in one piece with the rotor of the individual driving motor, which is of the induction type rated at 40 watts, and runs at 12,000 r p.m. In operation the package is entirely enclosed by a domed cover which fits into the base of the package carrier A, and prevents the ballooning thread from fouling the package. The main application of this spindle is at present for continuous filament rayon.

Control by Eccentric Axes, etc.

It is doubtful if the devices mentioned under this heading are of more than academic interest, and for that reason they will not be described at length.

Dunn[2,3] besides using gear and friction wheels for his spindle patented in 1861, invented an arrangement comprising an oscillating catch and two stops, the catch was attached to the creel and operated by a cam centred on the spindle As the spindle revolved the catch was thrown into contact alternately with the opposed stops on each side of the spindle, but always in the position opposite to the single sided flyer; thus the creel was at all times engaged with one of the stops to prevent rotation and the flyer revolved without interference In 1890 Golding[11] patented the idea of mounting the package carrier within a flyer carried by spindles with eccentrically placed axes The same method was employed 34 years later by Leconte.[21] This spindle (Fig. 17) consists of a frame A carrying the bobbin B, freely mounted on rotary shafts C,D mounted eccentrically to each other The shaft C is driven by a pulley E and rotates the shaft D through arms F connected by a thread, cord or wire G The small frictional torques exerted by spindles C and D tend to rotate frame A about different centres. This tendency is opposed by stresses in the frame which supply the restoring couple necessary to maintain the frame stationary.

OTHER METHODS OF INSERTING MULTIPLE TWIST

Up to this point double-twist spindles alone have been dealt with and although such mechanisms vary in constructional detail the basic principle is common to all types There are, however, other methods of inserting multiple twist which, whilst not conforming to the true double-twist principle, may conveniently be considered very briefly at this stage They may be classified as:—

(a) "Double Motion" Spindles.
(b) Rotating Creel

Double Motion Spindles

With this type one or more rotating flyers or spindles is (or are) rotated bodily about a common axis. Saracco's[17] patent of 1909 specified a multiple spindle for silk wherein the first twisting, doubling and second twisting are combined in a single operation Two bobbins B,B_1 (Fig 18) are rotated around their own axis in a direction contrary to that in which they rotate round a common axis This is achieved by the casing C, which encloses the bobbin gears DD_1, being rotated by pulley E, while the central wheel F is fixed to stationary shaft G, the gears DD_1 engaging the central gear F through carrier pinions, which for clarity are not shown in the diagram. The yarns are first twisted separately on their individual spindles, and then passed through eyes of flyer H by which they are doubled and twisted together.

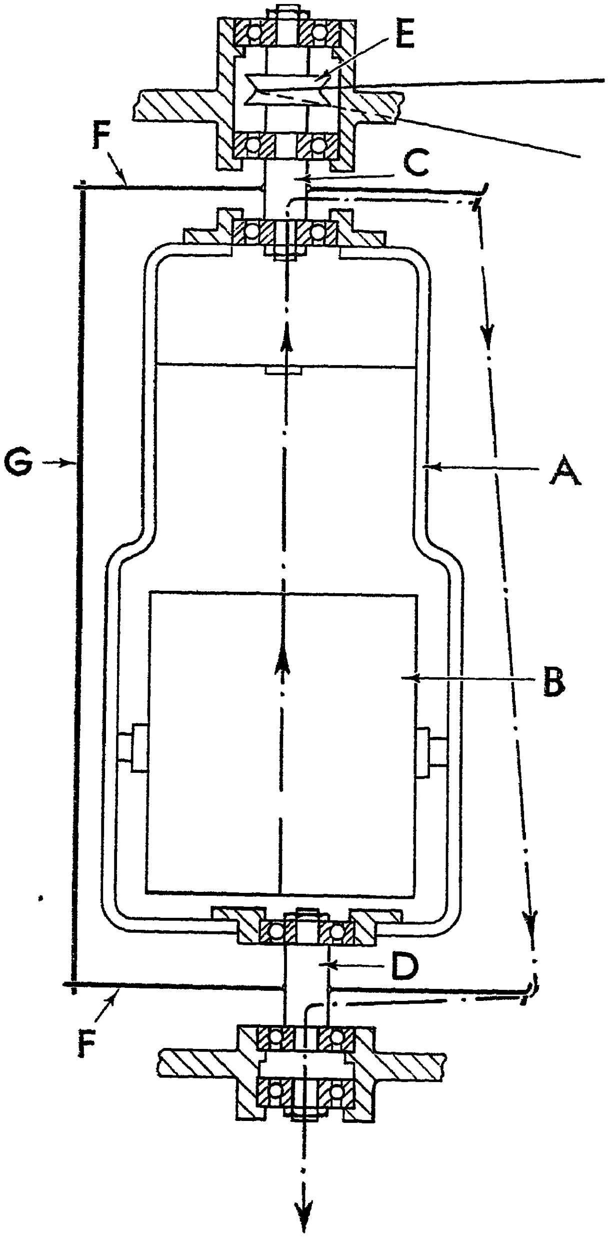


Fig 17.
(Leconte, 1924)

An early spindle of this type is one patented by Hird[4] in 1878. A double motion is imparted to a spindle of the flyer category—one round its own axis and the other round a fixed axis about which the flyer is rotated bodily after the manner of a sun and planet gear train The twist inserted is equal to the sum of these two motions Similar in design to Saracco's patent but with friction discs in place of gears is a spindle patented by Woosnam[19] in 1913.

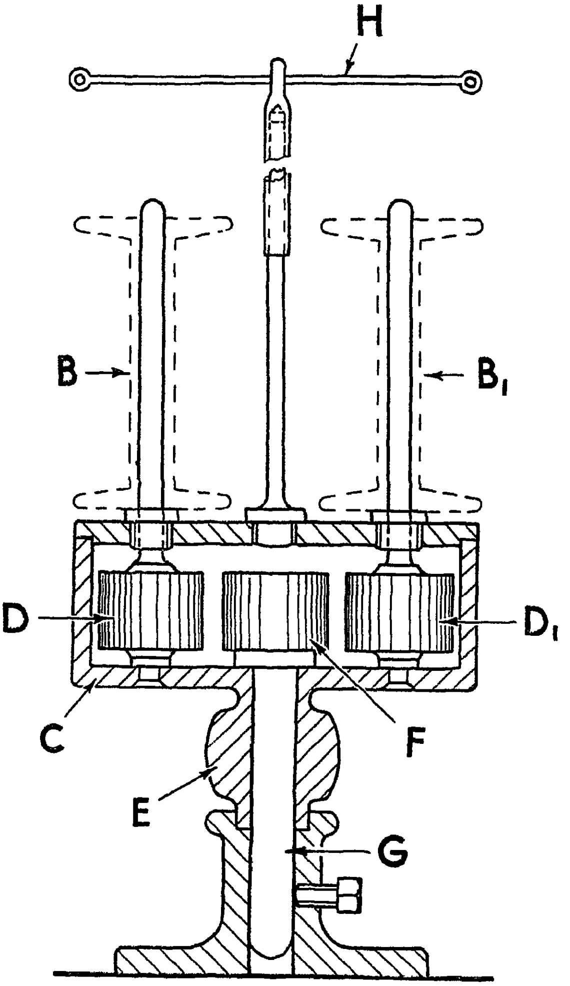


Fig 18.
(Saracco, 1909)

In general, spindles of the double motion type are intricate and bulky; their main industrial application appears to be in the manufacture of ropes and hard-twisted cords.

Rotating Creel

This type of twister combines up- and down-twisting, for both supply and take-up packages are rotated. Two spindles are required per "end" and the rate of twist insertion corresponds to the sum of the individual spindle speeds.

The principle, which is quite simple, is illustrated in Fig. 2 The creel package is placed on a revolving spindle A and the yarn is drawn off over guide B by rollers C which in turn deliver the yarn to a further twisting spindle D It will be seen from the diagram that the spindles both rotate in the same direction, but owing to the disposition of the spindles the twists inserted in the yarn are additive.

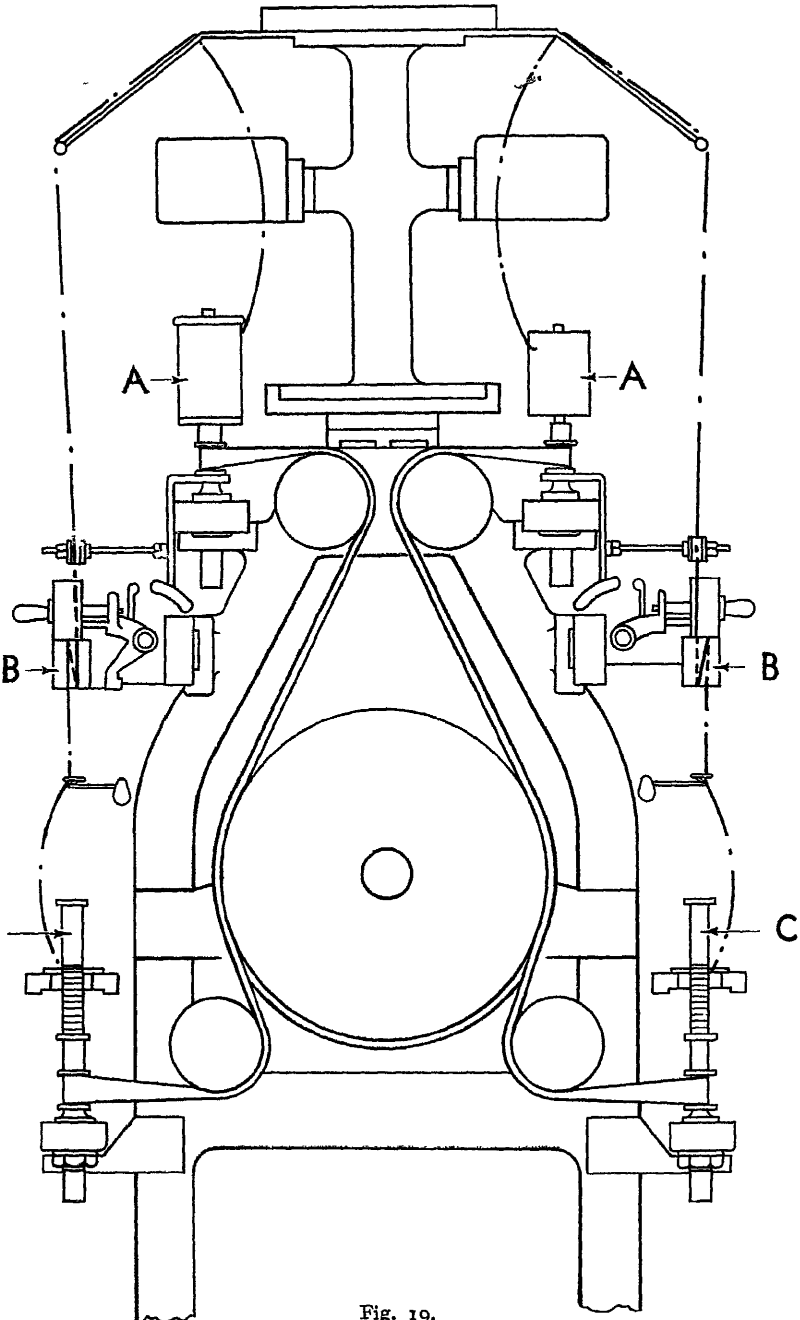


Fig. 19.
(Watson-Lister, 1932)

This method of dual-twisting found early application in an invention by Murray[5] (1879) wherein the yarn drawn off *two* rotating supply spindles passes through rollers and is doubled together by a third spindle. For a similar device Unsworth[8] uses flyer spindles, the supply spindles having an inverted flyer and the yarn passing over a rubbing roller and through a water trough before receiving the final twist. An example of the application of this system to a frame incorporating a ring spindle as the final doubler is given in an invention by Whyte[14] in 1904 and a similar arrangement was used by the firm Soie de Chatillon[28] in 1927. This combination of up-twister and ring spindle has been applied more recently to the "Watson-Lister" High Speed Twisting Frame[98] and the Dual Twister[95] of the Saco-Lowell Shops in the U.S.A. Fig. 19 illustrates the Watson-Lister machine. The supply package A is placed on the upper creel spindle, the yarn is drawn off by roller B and passes to a normal ring spindle C. The rollers B are arranged with their axes pointing outwards to facilitate threading and each pair is provided with a stop-motion. The Saco-Lowell Twister is very similar but a trough is provided for wet doubling and twisting.

APPENDIX

The only information concerning the performance of double-twist spindles operating on the large scale under mill conditions relates to the Dunlop spindle (Fig. 8). This is based on data (kindly supplied by Mr. Langstreth of Messrs. Dunlop Cotton Mills) obtained from the running of over 5,000 "old" type spindles for a period of over 60,000 hours and an approximately similar number of "new" type spindles running for over 40,000 hours. (The "new" type spindle incorporates improvements in the design of spindle, pendulum and "tall hat" bearings and means for preventing the accumulation of waste round that part of the spindle between the bearing and disc.) Maintenance and repair work consists chiefly of (*a*) lubrication of main bearings with grease after 1,200 running hours and lubrication of pendulum bearings with a mixture of sperm and spindle oils after 200 hours; (*b*) replacement of flannel drag washers every 1,600 hours, (*c*) replacement of worn spindle and pendulum bearings, the average life of a spindle of the new type being over 120,000 hours. The range of resultant yarn count handled is from 3s to 5s, but experimental doublings have been made on 40s/2 and 40s/2/2. Twist multipliers used range from 4 to 14. The spindle package is a precision-wound cheese weighing approximately one pound, although a spindle is being developed to carry a much larger package. The delivery package is a double-flanged bobbin containing 5¼ lb. of folded yarn.

Claims are made for very high plant efficiency, full ultilisation of labour, and increased regularity of product and production over the conventional ring doubler.

REFERENCES

Below is appended a list of English and foreign patent numbers, giving the name of the patentee, the subject of the patent and year, also a list of articles that have appeared in British and foreign textile periodicals on the subject of double-twisting.

British Patents with Reference to Double Twist Spindles

Ref. No.	E.P.	Patentee	Subject of Patent	Year
1	1,711	Kirkman, C. F.	D.T. spindle	1855
2	846	Dunn, J.	" "	1861
3	1,563	Dunn, J.	" "	1861
4	3,847	Hird, E.	"Double-motion" spindle	1878
5	296	Murray, W.	Rotating creel	1879
6	2,351	King, J.	D.T. spindle	1880
7	1,855	Clegg, R., and Taylor, J.	" "	1881
8	7,450	Unsworth, T.	Rotating creel	1884

Ref. No.	E P	Patentee	Subject of Patent	Year
9	10,367	King, J.	D.T. spindle	1885
10	1,383	Shepherd, J W , Ayrton, W , and Clegg, R	,, ,,	1886
11	5,887	Golding, W	D.T spindles and accessories	1890
12	26,921	Beck, J. H.	D.T. unit	1898
13	12,940	Fahr, J G	,, ,,	1903
14	12,577	Whyte, J D	Rotating creel	1904
15	14,006	Mathewson, A L , and Barney, C W	D T spindle	1904
16	3,011	Bebié, E	,, ,,	1907
17	10,857	Saracco, P	" Double-motion " unit	1909
18	12,864	Norman, T W , and Delaney, R.	D T unit	1912
19	1,448	Woosnam, A	" Double-motion " unit	1913
20	20,492	Brevetti Saracco	" Double-motion " spindle	1914
21	242,943	Leconte, G	D T. spindle	1924
22	267,839	Howard & Bullough, Ltd Bancroft, J	,, ,,	1926
23	287,202	Dunlop Cotton Mills, Ltd Andrew, T E , and Langstreth, M.	Tensioning and bobbins	1926
24	287,338	,,	D T. spindle	1926
25	287,334	,, Howard & Bullough, Ltd. Bancroft, J	,, ,,	1927
26	292,076	Baudonnel, V , and Berthier, J	,, ,,	1927
27	298,938	Masson, L. M	,, ,,	1927
28	299,031	Soie de Chatillon	Rotating creel	1927
29	299,860	Durand, M P	D T spindle. Magnetically-held package	1927
30	300,134	,,	Tensioning regulator	1927
31	300,484	,,	D T spindle Magnetically-held package	1928
32	324,544	Société d'Applications Générales d'Electricité et de Méchanique	D T spindle Creel held by gear train	1928
33	324,566	,,	,,	1929
34	331,702	Berthier, J., and Baudonnel, C V	D T spindle Electric stop-motion applied	1929
35	338,570	Dunlop Cotton Mills, Ltd Andrew, T. E , and Langstreth, M	D T spindle	1929
36	338,606	,,	Tensioning methods	1929
37	345,139	Kraft, J	D T. unit for wire ropes and strands. Two concentric flyers	1930
38	345,504	Fener, B.	D.T spindle Winding on to spindle package	1929
39	358,827	Barmer Maschinenfabrik A -G	Yarn tensioning device	1931
40	361,373	Dunlop Cotton Mills, Ltd Andrew, T E , Langstreth, M	Adaptation for fancy yarns	1930
41	361,792	Barmer Maschinenfabrik, A -G	Thread " storing device "	1931
42	362,310	,,	,, ,, ,,	1931
43	365,266	Dunlop Cotton Mills, Ltd Andrew T E , Langstreth, M	Adaptation to take cops, etc	1930
44	365,437	Barmer, Maschinenfabrik, A -G	Whorl and disc made in one piece	1931
45	368,200	,,	Double-twisting frame	1931
46	368,577	Fener, B	(additional to 345,504)	1931
47	369,293	British Celanese, Ltd. Pool, W	D T spindle Creel held by friction rollers	1930
48	369,939	,,	Two threads off one package	1930
49	369,940	,,	Adaptation for fancy yarns	1930
50	369,433	Barmer Maschinenfabrik, A -G	Disc replaced by dome	1931
51	377,113	,,	Guiding element fixed to bobbin carrier	1932
52	377,125	,,	Storing-ring extended	1932
53	377,130	,,	Extended insert for larger bobbins	1932
54	380,708	,,	Weight modifications	1932
55	380,713	,,	,, ,,	1932
56	381,878	,,	Spindle adapted to carry two or more bobbins	1932

Ref. No	E.P.	Patentee	Subject of Patent	Year
57	381,885	Barmer Maschinenfabrik, A -G.	Guard disc modifications	1932
58	382,179	,,	Weight modification	1932
59	388,078	British Celanese Ltd	Yarn tensioning device	1931
60	388,406	,,	Combined twister and warper	1931
	388,407	,,	Combined twister and winder	1931
61	400,867	Barmer Maschinenfabrik, A -G	Double-twisting frame	1933
62	404,168	Soc Italiana Pirelli	D T spindle, and unit of three	1933
63	404,915	,,	Multiple double-twist unit	1933
64	406,801	Soc Textile Twistock	D T spindles with electric stop arrangements	1932
65	406,806	,,	,,	1932
66	415,635	Soc Italiana Pirelli	Light flyer device	1933
67	420,058	Barmer Maschinenfabrik, A -G	Spool holder for cops	1934
68	424,278	British Celanese Ltd Pool, W	Modified friction roller arrangement	1933
69	427,240	Barmer Maschinenfabrik, A -G	Thread clearer	1934
70	430,537	,,	Yarn guide	1934
71	432,170	,,	Spindle modifications	1935
72	443,352	,,	Spherical yarn guide	1935
73	472,998	,,	Method of mounting spindle and driving arrangement	1936
74	490,998	,,	Arrangement for drawing off and winding	1938
75	492,238	,,	Arrangement to facilitate threading	1938
76	494,753	Comptoir de Materiel Textile	Double-twisting frame	1937
77	498,693	Dunlop Cotton Mills, Ltd Langstreth, M, and Townson, F. R	D T spindle	1937
78	499,624	Kent, F J	D T spindle with electric motor drive	1938
79	505,345	Barmer Maschinenfabrik, A -G	Thread engaging device	1938
80	572,026	United States Rubber Co	D T spindle, used for folding yarns	1945

Foreign Patents

Ref No	Patent No.	Patentee	Subject of Patent	Year
81	D R P 577,911	Meyer, A	D T spindle	1931
82	D R P 594,459	Barmer Maschinenfabric, A -G	Sizing or wetting device	1932
83	U S P 2,233,645	Atwood Machine Co	D T spindle	1940
84	U S P 2,374,085	Saco-Lowell Shops Gwaltney and Marsh	D T spindle Magnetically held package	1943
85	U S P 2,379,806	Kent, F J	D T spindle	1944
86	Brevet français 913,970	Société Rhodiacéta	D T spindle Package rotated	1946 (?)

References to Literature

87 A patent Double Twist Machine *Textile Mfr*, 1929, **55**, 237

88 " Nouvelle méthode de retordage des fils " *Revue Textile*, 1929, **27**, 165.

89 A Double Twist Doubling Machine *Textile Mfr*, 1930, **56**, 98.

90 A New Doubling Machine *Textile Recorder*, 1930, **47**, No 564, p 42

91 Brevet français No 682,486 *Revue Textile*, 1930, **28**, 1391

92 Hill, H A New Double Twisting Frame *Textile Weekly*, 1931 ,**6**, 580

93 de Prat, D " Durand and Masson Double-Twist Twisting or Doubling Frame " *Textile Mfr*, 1931, **57**, 326

94 Petit, L " Nouvelle methode de torsion au moulinage " *RUSSA*, 1932, **7**, 645

95 Saco-Lowell Bulletin. 1932, Sept /Oct, 12

96 " Über die Erzeugung von Doppeldraht " *Spinner u Weber*, 1933, **51**, No. 26, 1

97 Woods, H J " The Kinematics of Twist " *J. Textile Inst*, 1933, **24**, T317.

98 " Watson-Lister " High Speed Twister *Textile Mercury*, 1934, **91**, 149

99 Same article as Ref 96 *Textile Lloyd*, 1935, **9**, No 6, 19

100 Constant, J " Elements d'étude sur la double torsion " *RUSTA*, 1935, **10**, 463, 521

101 Colin, J A. " Observations sur la broche à double torsion." *L'Industrie Textile*, 1937, **54**, 118, 166

102 Ashworth, C "Doubling Principles and Machines" *Textile Recorder*, 1934, **52**, No 617, 22, No 619, 28

103 Schmid, E "Das Zwirnen ohne Ring oder Flügel" *Textilberichte*, 1934, **15**, 99.

104 Bailey, W "Twisting and Doubling Machines Developments" *J. Textile Inst*, 1935, **26**, P 147

105 Colin, J A "Alcune Note sulla Fabricazione dei Ritorti per Pneumatici" *Bolletino della Cotoniera*, 1937, **32**, 489

106 Production of Tyre Cords *Textile Mercury*, 1938, **98**, 722

107 Tyre Cord Production *Textile Weekly*, 1938, **21**, 758

108 "A Double Twist Twisting Machine" *Textile Weekly*, 1938, **22**, 16

109 "Une broche a retordre à double torsion" *Revue Textile*, 1939, **37**, 461

110 A Survey of the German Cotton, Rayon and Silk Industries B I O S Final Report No 574, Item Nos 22 and 31, p 24

111 "Electrification of the 2-for-1 Twister" *Electrical Engineering* (Amer), May/47, 474-6

112 "Augmenter la production au moulinage" *L'Industrie Textile*, March, 1947, No 724, p 56

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17—THE TESTING OF SIZES FOR CONTINUOUS FILAMENT YARNS OF HIGH FILAMENT STRENGTH

By E. Bradbury

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SUMMARY

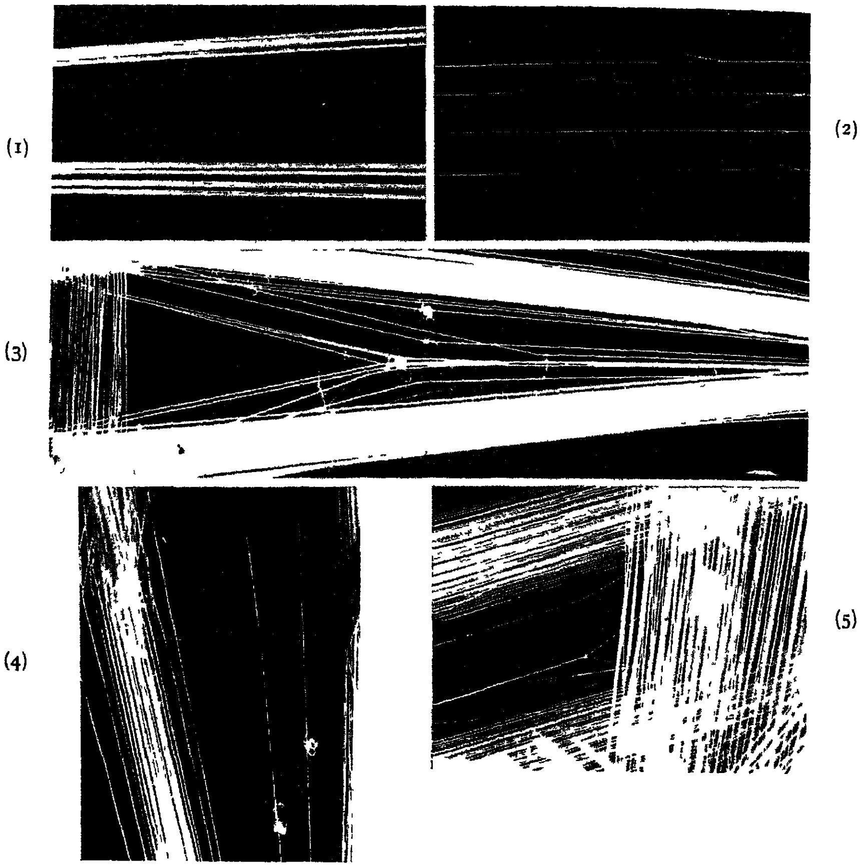
Two rapid small-scale methods are described for assessing the weavability of sized continuous filament yarns of high filament strength, such as nylon The Tape Weavability Test is an accelerated weaving test on narrow warps, in which potential sources of weaving troubles are created in a more frequent and regular manner than would obtain in a normal warp, by cutting single filaments on one or more threads at the back rest of the loom The ability of the sizing treatment to prevent cut filaments from causing trouble (such as thread breakage or further filament breakage) is closely related to its function in normal weaving The Single-thread Filamenting Test measures the tendency of a cut filament to peel away from the parent yarn under the influence of bending and rubbing against suitable surfaces, and provides an index of one of the most important aspects of the weaving behaviour of yarns of high filament strength The test is best used as a rapid sorting test to weed out unsuitable sizes, as a preliminary to the more thorough examination of the more promising sizes by the Tape Weavability Test

INTRODUCTION

In the investigation of the effect of warp sizes on the weaving behaviour of continuous filament yarns the direct method of the full-scale sizing and weaving trial is usually adopted Whatever the advantages of this method it has the serious drawback that it is expensive in material and time, and is therefore unsuitable when the weaving possibilities of a large number of sizes have to be examined Where synthetic yarns of high filament strength, such as nylon, are concerned, the Tape Weavability Test and the Single-thread Filamenting Test are more rapid and economical means of roughly assessing weavability and have proved of value as sorting tests in the investigation of sizes for these yarns

The Tape Weavability Test is an accelerated weaving test making use of narrow warps two inches wide, and is closely related in nature to weaving under normal conditions The Single-thread Filamenting Test, as the name implies, involves the testing of single threads, and is even more rapid and economical in material than the previous test It is concerned with only one of the many factors involved in the weaving process, but in the weaving of yarns of high filament strength this factor is usually the predominant one, and when this is so, the test apparently provides a rough index of the weavability of such yarns Its more general application is as a sorting test to weed out unsuitable sizes, since it is a more reliable index of bad than of good weaving Any size mixture giving good results on the Filamenting Test is then tested more thoroughly by the Tape Weavability Test and, if still satisfactory, is given a full-scale sizing and weaving trial. The application of these tests to yarns of lower filament strength (e g viscose and cellulose acetate yarns) has not been thoroughly explored, but it is evident that their interpretation in terms of weaving behaviour will be more complex than with the stronger filament yarns

In the following sections the defects associated with filament breakage that occur in the weaving of a warp are first described, and descriptions of the two tests are then given, followed by some evidence of the validity of the results of these tests as indexes of the weaving behaviour of yarns of high filament strength.



Figs. 1-5

FIG 1. Broken filaments peeling away from the parent yarns between lease rods and healds.

FIG. 2 Threads partially cut through by broken filaments on adjacent yarns.

FIG. 3. Complex entanglement formed by broken filaments between lease rods and healds.

FIG 4 " Beads " formed on two threads between healds and reed.

FIG. 5 Broken filament peeling from parent thread and forming a " bead " locking together two adjacent threads behind the healds

FILAMENT BREAKAGE IN THE WEAVING OF CONTINUOUS FILAMENT YARN

In the weaving of yarns with comparatively strong filaments such as nylon, observation suggests that a large proportion of the warp troubles arise from filaments broken in previous processing. Some of these are seen as entangled masses on the yarn as it comes up from the beam, but others are not always so easily visible, and their presence is detectable only when they pass the lease rods and reach the region where the threads are crossing to form the back shed As the broken filament weaves up from the beam its behaviour depends to a marked degree on the type and amount of size on the warp. If the filaments are only weakly bound together by the size, the broken filament may begin to peel away from the parent yarn in the region between lease rods and healds (Fig 1). If the size is "strong" enough to prevent the filament peeling behind the healds it may fail in the healds, or in the reed where the abrasive action is more severe, or peeling may be prevented entirely and the filament may weave into the cloth without causing trouble

The effect of the peeling filament on adjacent threads again depends on the sizing treatment If the size is deficient in lubricant, broken filaments projecting from the thread show a marked tendency to cut adjacent threads in the region of the shed. The effect is a remarkable one, and looks as if a sharp razor had been drawn across the thread opposite to the broken filament (Fig. 2). The incidence of this type of damage can be considerably reduced by the presence of a suitable lubricant in the size, but even so the broken filament can form a more or less complex entanglement depending on the ease of peeling (Fig. 3), and can cause breakage of other filaments and yarns by this means, although weaving may go on for some time before breakage actually occurs This type of damage occurs with and without lubricant but is reduced when a suitable lubricant is present If the broken filament becomes entangled with adjacent threads between healds and fell, floats in the cloth are commonly caused. Sometimes the entanglement is only temporary and no breakage of other filaments occurs, but the effect is undesirable nevertheless, as floats are considered serious cloth defects. With some sizes broken filaments show a tendency to form "beads" either behind the healds or behind the reed (Fig. 4). If the bead forms on the parent thread only, it may continue to build up indefinitely until it is removed or it may weave through into the cloth. The bead sometimes forms round the parent and one or more adjacent threads, or round threads adjacent to the parent thread (Fig 5). It may lock them firmly together, and continue to build up until the threads are broken

Another possible defect associated with the warp is the deposition of size from the warp on the various parts of the loom This may or may not be serious, depending on the nature, amount and location of the deposit; a hard or sticky deposit in the reed may eventually cause filament breakage if it builds up sufficiently, but a light dry size dust in the healds and reed may do no harm.

It is evident that with strong filament yarns it is of the first importance to prevent any broken filament from peeling away from the parent yarn, and a suitable size for such a yarn must at least perform this function. In addition the size should, either by suitable lubrication or otherwise, protect a yarn against damage by broken filaments or by contact with the parts of the loom.

In the weaving of continuous filament yarns of lower filament strength, such as viscose and cellulose acetate yarns, the issue is more complex. Whereas with the types of yarn discussed above, a peeling filament is an almost certain source of trouble necessitating attention by the weaver, with acetate yarn in particular it may not be so because the filament may break off before it damages adjacent yarns. A badly filamented patch in a suitably sized acetate warp may clear itself without attention from the weaver through the filaments breaking off, but a similar patch on a nylon warp would become rapidly worse if weaving continued.

THE TAPE WEAVABILITY TEST

This test is a small-scale weaving test in which one or more filaments are purposely cut on the warp at the back rest of the loom in order to provide potential sources of trouble in a more frequent and controlled manner than would normally occur in a sized continuous filament warp. As the cut filaments weave through to the front of the loom, observations are made of their behaviour and their effect on adjacent yarns and filaments. Experimental details are given below.

Warps are sized on a small-scale cylinder sizing machine with the mixings it is required to compare and wound on to flanged beams two inches wide. The warp length is usually about 50 yd. and the number of ends such as to give a width in the reed of about 1¾ inches for the particular cloth under investigation. About nine such warps, individually tensioned, are mounted side by side in a full-scale loom with a special selvedge warp (usually cotton) in the outer position at each side. All warps are woven with a common weft which is allowed to form floats between the warps from the several beams.

After carefully examining the length of warp in the loom to ensure that it is free from broken filaments, single filaments are cut on each of three threads equally spaced in each warp The threads carrying the cut filaments are marked with ink about 12 inches behind the back rest and another mark on the edge of the warp opposite the cut filament indicates its position along the length. The cutting of the filament is done by a pair of suitably modified scissors. One of the blades, containing a fine notch, is drawn transversely across the thread until a single filament is held by the notch away from the parent thread, and the filament is then cut by bringing the other blade across. If the filaments are cemented together very firmly by the size a localised rubbing with a suitable smooth instrument may be necessary to break down the size film and enable a filament to be isolated. It may also be necessary to use a fine dissecting needle under a magnifying glass to secure the separation of the filament before cutting.

As the cut filaments weave through the loom they may cause trouble of various kinds which is carefully recorded at the time and classified as follows:

(1) *Actual or potential break.* These include breaks in the parent or adjacent threads, and filamenting of parent or adjacent threads of such a nature that (at her own discretion) the weaver is obliged to cut out to avoid further trouble. Any of the occurrences shown in Figs. 1, 2, 3 or 5 would be classed as a potential break.

(2) *Floats.*

(3) *Residual filamenting.* When the position of the original cut filament has woven 10 inches beyond the fell of the cloth the warps are carefully examined from fell to back-rest for any broken filaments remaining on the threads.

Residual filamenting is serious or not depending on whether it is likely to cause trouble in further weaving A reliable decision on this point can only be made after some experience of the weaving of the type of yarn under examination, and standards may vary from one type of yarn to another. For nylon the residual filamenting is considered serious if it includes beads or entanglements, or if more than one thread is filamented, or if any projecting filament is greater than one inch in length

After the test is finished any warps containing residual filaments are drawn through the loom until a clean filament-free length is available for the next test, when the above procedure is repeated. Ten or more tests are done on each warp, and for each warp the number of "trouble free" tests expressed as a percentage of the total number of tests is called the "Tape Weavability". A "trouble-free" test is defined as one in which neither actual nor potential breaks, floats, nor serious residual filamenting occur. With this method of expression of weaving behaviour a high value (e.g. a Tape Weavability value of 100 per cent.) indicates good weaving, in contradistinction to the more usual method of expression in terms of a warp breakage rate.

In order to compare warps of very high or of very low values of Tape Weavability it may be necessary to alter the stringency of the test. As an example, a number of warps may have zero Tape Weavability under the above conditions, and in order to establish differences between them it would be necessary to make the test less severe. The stringency of the test can be altered either by cutting more or fewer filaments, by suitably adjusting the standards of tolerance in the definition of "serious trouble", or by increasing or reducing the picks per inch in the cloth. If the object of the experiment is to investigate sizes for a particular cloth, the last mentioned alternative is obviously the least desirable.

In addition to the filamenting and breakage of warp threads, any other features of interest are noted, in particular the deposition of size on the parts of the loom.

As with other weaving tests it is inadvisable to judge the behaviour of any size mixing from its performance on a single warp, and at least two warps should be examined, preferably from different preparations of nominally the same mixing.

THE SINGLE-THREAD FILAMENTING TEST

It has been stated that, with yarns of high filament strength, a peeling filament is an almost certain source of trouble in the loom necessitating attention by the weaver If the tendency of broken filaments to peel were the only factor involved in the occurrence of trouble, then a numerical measure of this property might be expected to correlate directly with the *number* of occasions of trouble during the weaving of a warp. It is highly probable, however, that other factors are involved that influence the frequency of occurrence of trouble, in addition to any effect they may have on the nature of the trouble As an example, a short projecting filament deficient in lubricant may cut adjacent threads, whereas one of the same length suitably lubricated may cause no trouble The influence of these other factors on the frequency of occurrence of trouble would be expected to be important only when the tendency to peel is small, since a yarn that peels easily will give trouble in any event. In the investigation of sizes for a particular yarn a measure of the tendency to peel would thus be of value as a means of weeding out unsuitable sizes, a value indicating a high tendency to peel would be a reasonably certain indication of bad weaving, although a low tendency to peel would not necessarily indicate good weaving, and would involve further trials using the more comprehensive Tape Weavability Test

The Single-thread Filamenting Test is intended as a rapid means of measuring the tendency of a cut filament to peel away from the parent yarn under the influence of rubbing and bending forces. The forces causing the filament to peel in the loom could only be reproduced by a system similar to the loom set-up, and in a test making use of any simpler arrangement there is a danger that the "peeling forces" in the test may not be sufficiently closely related to those in the loom to give results of value as an index of weaving behaviour Although the conditions in the test described below have been chosen in an arbitrary manner, and there is no reason to suppose they are the best possible for the purpose, evidence is given later to show that the test is a reasonably good index of those aspects of weaving behaviour that depend on filament peeling in the loom.

The apparatus is illustrated diagrammatically in Fig. 6. Ten threads are tested side by side but the diagram is a side view and shows the set-up for a single thread.

A movable carriage A, to which one end of the thread under test T is attached by means of a screw grip H, is driven backwards and forwards in a horizontal plane by means of the connecting-rod fixed to the wheel B of 2 inches effective radius making 80 revolutions per minute. The thread under test passes over stainless steel guide rods of ¼ inch diameter and through a needle puncture in a thin rubber sheet E placed in a vertical position between them. The thread is weighted by a total load of 18 gm., and this includes a device involving the use of two supporting strings operating in glass tubing guides F to prevent the thread untwisting. The rubber sheet E is 0·25 mm. thick and is bought as "Dental Rubber Dam". It is cut in the shape of a disc with a hole in the centre and held in position by clamping between the rotatable brass disc G and the brass strip J (see Fig. 7)

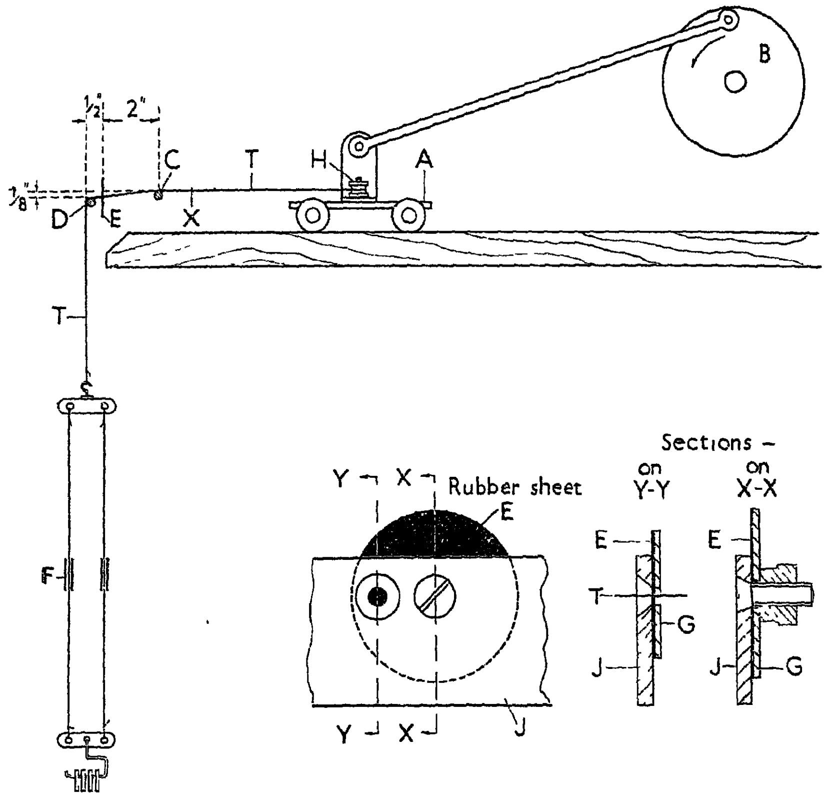


Fig 6

Fig 7

When the test is in progress the ⅛-inch hole near the periphery of the brass disc G is always superimposed on that of similar dimensions in the brass strip J so that a circle of rubber of ⅛ inch diameter is left exposed on both faces The centre of this circle is in line with the upper surface of the guide rods C and D Similarly it is in line in a vertical plane with the screw grip H and the upper hook on the weighting attachment This ensures that the tendency of the thread to enlarge the needle puncture in the rubber is at a minimum.

In threading up the machine a sharp needle (of 0·7 mm. diameter just below the eye) carrying the thread is passed through the centre of the exposed circle of rubber and the thread is pulled through and attached to grip H.

With the connecting-rod at back-centre a single filament is cut in the thread at the position X ¾ inch behind the rod C. The cut filament is then peeled back until its point of junction with the parent yarn is immediately above the rod C, and the projecting part trimmed to a length of ½ inch. Ten threads are treated side by side on the machine in this manner. The machine is then run for a predetermined number of revolutions of the wheel B and is stopped with the connecting-rod at back-centre. The threads are then carefully examined, and notes made of the number of threads where the cut filament has either broken off, or peeled away from the parent yarn for a distance of 2 inches, so that it is held up by the rubber sheet. Sometimes the cut filament forms a little ball or bead on the yarn behind the rubber sheet and the presence of these is noted. The machine is then run for a further period, the threads are re-examined and so on, until all the threads have suffered either filament breakage or peeling over a distance of 2 inches.

The method of selecting and cutting the single filament is as described for the "Tape Weavability" test, and whatever the method used, the filament is peeled back to the "zero" position C out of range of the length of yarn disturbed by the selection and cutting procedure.

Of the yarns tested in this way only cellulose acetate and viscose have shown filament breakage in addition to filament peeling and these will not be considered further in this paper. Where filament peeling only takes place the results are grouped in the form of a frequency distribution with the logarithm of the number of rubs[*] as the variate. The mean value of log rubs required to cause filament peeling over a length of 2 inches is calculated and referred to as the "Resistance to Filamenting". As an illustration, the results obtained on a sample of 50 nylon threads are given in Table I. The machine was stopped for examination of the threads after 25, 50, 100 rubs and so on, until all the threads had peeled. The raw data are tabulated in the first two columns. It is obvious from the data that a frequency distribution of peeled threads with the number of rubs as variate is not symmetrical. Accordingly, if the mean number of rubs required to cause peeling were used as a measure of the Resistance to Filamenting it would be affected unduly by the relatively small number of extremely high values of rubs. However, if the logarithm of the number of rubs is taken as the variate (column 3) the frequency distribution is then approximately normal and the mean log. rubs is probably the best single estimate of Resistance to Filamenting. This is calculated in the usual manner as shown in the Table.

Table I.
Filamenting Test on 50 Nylon Threads.

(1) Number of rubs	(2) Number of threads peeling within these limits	(3) Logarithm of rubs	(4) Mean values of log rubs from (3)	(5) (2) × (4)
25– 50	2	1·40–1·70	1·55	3·1
50– 100	14	1·70–2·00	1·85	25·9
100– 200	14	2·00–2·30	2·15	30·1
200– 400	16	2·30–2·60	2·45	39·2
400– 800	3	2·60–2·90	2·75	8·2
800–1600	1	2·90–3·20	3·05	3·0
Total	50			109·5

$$\text{Resistance to Filamenting} = \frac{109\cdot 5}{50} = 2\cdot 19$$

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[*] One revolution of the wheel B is referred to as one rub.

When the cut filament forms a bead on the yarn this does not affect the expression of the results in terms of Resistance to Filamenting since the filament is still present on the yarn and in the absence of other evidence the position of the bead is taken as indicating the point of junction of the cut filament with the parent yarn. The number of threads in which beads occur, expressed as a percentage of the total tested, is referred to as "Percentage Beading". This value provides some information of the nature of the troubles likely to be encountered in weaving.

Effect of Conditions of Testing

Before the conditions of testing described above were decided upon the effect of varying some of the conditions was investigated.

Resistance to Filamenting falls as the weighting on the yarn is increased as is shown by the figures for a sized nylon yarn in Table II.

Table II
Effect of Thread Weighting on Resistance to Filamenting
[Yarn 45-den nylon, sized.]

Weight (gm) .	18	30	40	50
Resistance to filamenting	2·18	2·00	1·87	1·74

The weight of 18 gm. was finally chosen for the test as being about the minimum that could be used to ensure smooth passage (i.e. without jerking) of the thread through the rubber sheet when the weight was moving downwards, and having also in mind the object of making the tests reasonably sensitive in order to cater for sizes of low "binding power".

Although no investigation of the effect of the diameter of the guide rods has been made with the existing set-up there is no doubt that they will have some effect, since when yarns were rubbed directly over glass rods of different diameters (i.e. in the absence of the rubber sheet) the Resistance to Filamenting increased with the diameter of the rod.

The effect was investigated of varying the diameter of the needle used to puncture the rubber sheet, and also of varying the thickness of the rubber. The results are given in Table III.

Table III
Effect of Needle Diameter and Thickness of Rubber on Resistance to Filamenting.
[Yarn 45-den nylon, sized.]

Thickness of rubber sheet (mm.)	Diameter of needle (mm.)			
	1·13	0·93	0·67	0·42
0·25	1·88	—	1·80	1·77
0·50	1·42	—	1·34	1·26
0·75	0·82	0·82	—	0·65

The effect of varying the thickness of the rubber sheet is considerable, Resistance to Filamenting falling with increasing thickness of rubber, but the effect of varying needle diameter is comparatively small. It was thought that more accurate means of making a hole of standard size and shape in the sheet might have to be devised, but since the effect of varying needle diameter is small, this is considered unnecessary and a simple puncture with a sharp needle is good enough. A needle of approximate diameter 0·7 mm. was chosen as standard on the grounds of convenience, and the thinnest rubber in order to give the test the maximum sensitivity.

The figures in Tables II and III are based on 50 single-thread tests under each condition and the general uniformity of the trends is sufficient evidence that reproducibility of results is good. If fairly large differences are being looked for in the evaluation of sizes, significant differences may be obtained on fewer measurements—say 10 or 20 per sample.

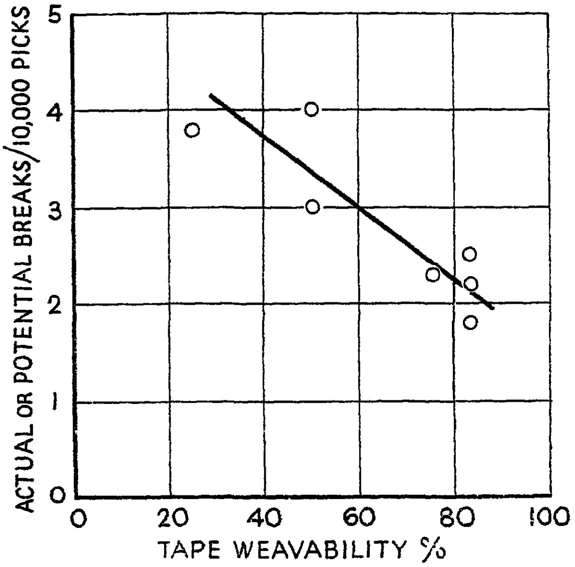

Fig. 8

THE VALIDITY OF THE TESTS AS A GUIDE TO WEAVABILITY

The chief evidence that the Tape Weavability Test is a reliable guide to large-scale weaving behaviour for strong filament yarns is that size mixings developed by its use have been found to behave as expected when used on the large scale. The only available data giving a direct comparison between Tape Weavability and large-scale weavability are given in Table IV and plotted in Fig. 8. The breakage rate in large-scale weaving is given as the number of occurrences of actual or potential breakage per 10,000 picks, it takes no account of the number of threads involved in a single occurrence of breakage.

Table IV

Tape Weavability and Warp Breaks in Normal Weaving.

[Cloth 120 ends per inch × 110 picks per inch, 45-den nylon warp and weft]

Warp No	Size mixing	% Size on yarn	Tape weavability (per cent)	Actual or potential breaks per 10,000 picks
NY28B	A	4.3	50	4.0
NY28A	A	6.0	83	1.8
NY29B	B	5.6	50	3.0
NY26C	C	5.8	83	2.5
NY26D	D	7.3	83	2.2
NY31	E	6.5	75	2.3
NY30	F	7.6	25	3.8

Taking into consideration the fact that none of the large-scale warps exceeded 50 yd in length and that the breakage rates quoted cannot therefore be very accurate, the degree of correlation is fairly good.

The Tape Weavability Test may not always give a sufficiently reliable estimate of the tendency of a size mixing to foul the loom since the length woven is too short. In large-scale weaving it has been found that a size deposit on the reed, for example, may build up slowly for a time until it reaches a condition of equilibrium beyond which no further apparent addition occurs and no damage is done to the yarn, whereas in the early stages the deposit may have looked serious.

For reasons already given the Filamenting Test on strong-filament yarns might be expected to correlate directly either with the Tape Weavability Test or with the breakage rate in normal weaving expressed as the number of occurrences of actual or potential breakage per 10,000 picks, only if the other factors influencing the frequency of occurrence of trouble either remained approximately constant or varied in close relation with the Resistance to Filamenting. Tables V to VII give results for three sets of warps, involving a fair range of types of size, where this condition was apparently realised, since good correlations were obtained. From this and other evidence it is inferred that the test is a good index of weaving behaviour for most of the sizes likely to be used. However, in a fourth set some warps containing a size of very tacky nature wove badly in the Tape Weavability Test, although Resistance to Filamenting was high, and it was evident that the Filamenting Test could not be regarded as a universal index of good weaving behaviour for all possible types of size. There was much cutting of adjacent threads by the short projecting filaments, suggesting that factors other than the tendency to peel were influencing the frequency of the occurrence of trouble. On the other hand, neither in this nor in any other set have warps in which Resistance to Filamenting was low woven well.

Tables V and VI give results for experiments involving a number of sizing treatments on synthetic yarns X and Y, respectively, in which both Tape Weavability and Resistance to Filamenting were measured. Filament denier and strength in grams per denier were, respectively, 2·5 and 3·3 for yarn X, and 2·5 and 4·9 for yarn Y.

Table V
Resistance to Filamenting and Tape Weavability
[Yarn 100-den. Synthetic X]

Warp No.	Size mixing	% Size on yarn	Resistance to Filamenting (log. rubs)	Tape Weavability (per cent)
NT516	G	5·7	1·60	100
NT517	G	3·9	1·40	50
NT518	G	2·1	1·00	0
NT519	H	4·5	1·56	80
NT520	I	2·6	1·23	30

Table VI
Resistance to Filamenting and Tape Weavability.
[Yarn · 100-den. Synthetic Y]

Warp No	Size mixing	% Size on yarn	Resistance to Filamenting (log rubs)	Tape Weavability (per cent)
NT556	J	14·3	2·00	58
NT557	J	14·9	2·12	58
NT558	J	12·5	2·37	83
NT559	K	13·0	2·38	83
NT560	L	7·8	1·60	0
NT561	M	12·0	2·03	67
NT562	N	12·4	2·53	83
NT563	N	11·6	2·26	83

Tape Weavability is plotted against Resistance to Filamenting for both sets in Fig. 9, and it is evident that a high degree of correlation exists between the two sets of figures Fig. 9 also illustrates the point that a particular value of Resistance of Filamenting may indicate good weaving on one type of yarn and bad weaving on another, so that a relationship can be expected only from data obtained on the same type of yarn weaving under the same conditions in the same cloth In starting any sizing investigation on a particular yarn and cloth, therefore, it will be desirable to find by weaving experiments the approximate level of Resistance to Filamenting required for good weaving.

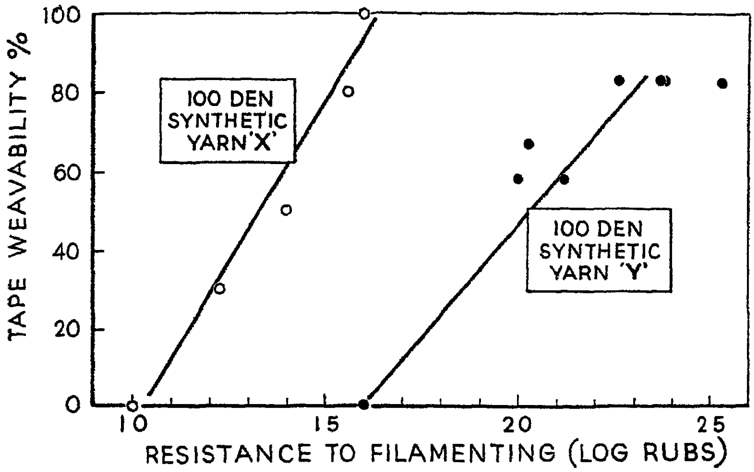

Fig 9

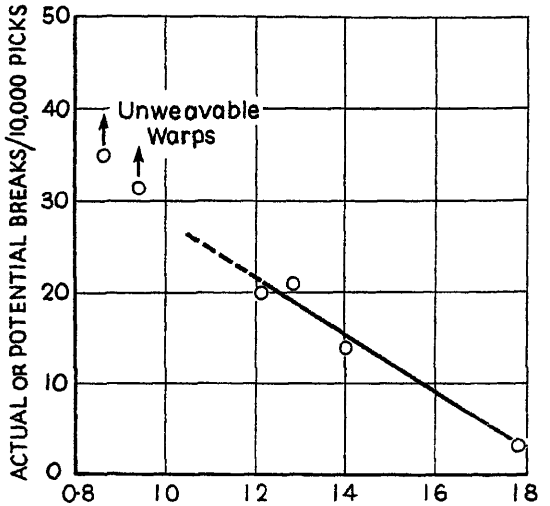

Fig. 10

Table VII gives results for an experiment involving the use of a number of sizing treatments on a badly filamented sample of synthetic yarn Y. The yarn already contained too many broken filaments for the Tape Weavability Test so an attempt was made to weave the narrow warps in the normal manner, and to record the number of occurrences of actual or potential breakage per 10,000 picks. In view of the badly filamented nature of the yarn, and the general unsuitability of the sizes, a substantial breakage rate was obtained even on these small-scale warps. The rate is plotted against Resistance to Filamenting in Fig 10, and again the degree of correlation is good

Table VII
Resistance to Filamenting and Warp Breaks in Normal Weaving.
[Yarn . 100-den. Synthetic Y]

Warp No	Size mixing	% Size on yarn	Resistance to Filamenting (log rubs)	Actual or potential breaks per 10,000 picks
NT550	O	8·5	1·78	3
NT551 .	P	10·4	1·21	20
NT552 .	Q	5·2	1·40	14
NT553	Q̃	4·4	0·86	Unweavable, worse than NT555
NT554 .	R	9·9	1·28	21
NT555	S	12·1	0·94	Unweavable

CONCLUSIONS

To sum up, it can be said that, on the evidence available, the Tape Weavability Test is a reliable index of the weaving behaviour of yarns of high filament strength such as nylon. The Single-thread Filamenting Test has proved a good index of weaving behaviour for most of the sizes examined covering a fair range of types, but is not an infallible index for all possible sizes. The evidence available suggests that a low value of Resistance to Filamenting is a reliable indication of poor weaving quality, but a high value does not necessarily indicate good weaving, and the test is best used as a rapid sorting test to weed out unsuitable sizes.

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18—THE ELECTRICAL RESISTANCE OF YARNS MADE FROM MIXED FIBRES, AND ITS USE IN MEASURING THE MOISTURE CONDITION OF THESE YARNS

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ABSTRACT

Initial assumptions are made concerning the resistance of a yarn of one type of fibre, the application of the parallel law of resistance to yarns of two types of fibres, and the relation between the individual and total moisture contents From these assumptions equations are derived which relate the resistance of a yarn of known amounts of two types of fibre to its total moisture content and to the properties of yarns made from the pure fibres. Experiments are described in which the resistances of yarns of cotton, viscose staple and wool and of yarns containing various proportions of cotton mixed with one of the other two fibres, are measured Reference is made to the effect on the resistance of the type of the electrode system, the voltage, and the method of mixing the fibres in the yarn. It is shown that there is good agreement between the theoretical equations and the experimental results The relation between resistance and relative humidity of the yarn is considered. A general equation for the resistance of a yarn of any number of types of fibre is given. Applications of the results to the Shirley Electrical Hygrometer and the Shirley Moisture Meter are discussed briefly. In an appendix, experiments to measure the resistance of viscose staple yarns and cotton yarns are described and an explanation is given of an apparent discrepancy between results in the present paper and those found in previous experiments.

INTRODUCTION

The Shirley Moisture Meter and the Shirley Electrical Hygrometer are instruments which have been designed by the British Cotton Industry Research Association to utilize the electrical resistance of textile materials as a measure of their moisture condition. The Moisture Meter has been described elsewhere[2]; the Hygrometer is similar in principle but the circuit has been arranged to cover a wider range of resistances in a large number of steps differing by only small amounts in the values of resistance which give a mid-scale reading on the milliammeter.

The Hygrometer was originally designed for use with running cotton warps after pure sizing at the tape-frame. The resistance of a length of warp is measured by means of suitably spaced electrodes. The following relation between the resistance and the equilibrium humidity of the yarn was found to hold:—

$$\log R = 8{\cdot}1 - \log\frac{E}{NL} - 0{\cdot}0715H$$

where R is the resistance in megohms, L is the length in inches, E is the number of ends, N is the count and H the percentage relative humidity.

The dial of the instrument is calibrated in Relative Humidity, and a calibration table is issued showing which resistance range should be used for any value of the warp-factor E/N, L being a constant for any one machine. The Hygrometer has since been applied to other materials and other drying machines and may indicate the moisture condition in terms of either equilibrium humidity, regain, or some convenient arbitrary standard. The Moisture Meter, originally designed for raw cotton or grey cotton yarn, can now be used to measure the moisture regain or moisture content of many textile materials in various forms such as cops, bobbins, beams and bundles of cloth.

Up to now the measurements made by both these instruments have, in general, been confined to materials consisting of one type of fibre only. In view of the increasing tendency to mix different kinds of fibres either by doubling of yarns or by mixing earlier in the spinning process, it was felt that there was a need to adapt these instruments to measure the moisture condition of mixed fibres. The investigation described in the present paper was carried out to see if any simple relation existed between the properties of a mixed yarn and those of its pure constituents. The knowledge of such a relation would make it unnecessary to calibrate the instruments empirically for every mixture on which they might be used.

The paper opens with the deduction of equations for the electrical resistance of a yarn of mixed fibres based on simple physical conceptions. The equation used for the resistance of a pure yarn is of the form given by Murphy and Walker[3] Walker has since pointed out[7,8] that, at very high or very low humidities, the equations which fit the experimental results are different. The present investigation has been limited to the middle range of humidities and it is shown that, within the limits of accuracy expected of the instruments, it is possible to apply the theoretically deduced equations. The paper concludes with an account of some practical applications of the results of the investigation

During the course of the experiments some apparently anomalous results were obtained for the electrical resistance of viscose staple yarn A description of further experiments and an explanation of the apparent anomaly are given in an appendix to the paper.

DERIVATION OF EQUATIONS TO BE TESTED

An equation, which was to be tested by experiment and which related the resistance of a yarn made of two types of fibre to its moisture content, was derived from the following initial assumptions —

(*a*) For a pure yarn, an expression given by Murphy and Walker,[3]

$$\log R = -n \log M + \log K \quad \ldots\ldots \quad (1)$$

or, in another form, $RM^n = K$ ....(1a)

where R is the resistance in megohms using a particular electrode system, M is the moisture content of the yarn

$$\left(\text{i.e., } \frac{\text{weight of moisture}}{\text{weight of undried sample}} \times 100\right) \text{ and } n \text{ and } K \text{ are constants.}$$

Since two types of fibre are being considered, let R_1, M_1, n_1 and K_1 and R_2 M_2, n_2 and K_2 refer to pure yarns of fibres 1 and 2 respectively; let R_m and, M_m refer to yarn containing a fraction a of fibre 1 and a fraction b of fibre 2.

(*b*) The parallel law of resistance

$$\frac{1}{R_m} = \frac{a}{R_1} + \frac{b}{R_2} \quad \ldots\ldots \quad (2)$$

(*c*) An additive law of moisture content,

$$M_m = aM_1 + bM_2 \quad \ldots\ldots \quad (3)$$

In addition, when the two types of fibre have come into equilibrium in a particular way at a particular relative humidity, we define a for those conditions of equilibrium and R H, as

$$a=\frac{M_2}{M_1} \quad \text{(4)}$$

In practice only samples which had come into equilibrium by absorption were tested.

From (1a) and (2),

$$\frac{1}{R_m}=\frac{aM_1^{n_1}}{K_1}+\frac{bM_2^{n_2}}{K_2}$$

$$\therefore \frac{1}{R_m}=\frac{aM_1^{n_1}}{K_1}+\frac{b(aM_1)^{n_2}}{K_2} \quad \text{from (4)}$$

$$\therefore \frac{1}{R_m}=\frac{a}{K_1}\left(\frac{M_m}{a+ab}\right)^{n_1}+\frac{b}{K_2}\left(\frac{aM_m}{a+ab}\right)^{n_2} \quad \text{since from}$$

(3) and (4) we have $M_1=\dfrac{M_m}{a+ab}$

By taking logarithms we obtain the general equation —

$$\log R_m=-\log\left\{\frac{a}{K_1}\left(\frac{M_m}{a+ab}\right)^{n_1}+\frac{b}{K_2}\left(\frac{aM_m}{a+ab}\right)^{n_2}\right\} \quad \text{(5)}$$

Two special cases of this equation are of interest in the present investigation.

(A) If an increase of the moisture content by a certain factor causes the same percentage decrease in resistance for each of the two materials, that is if $n_1=n_2=n$, we have —

$$\log R_m=-\log\left(\frac{M_m}{a+ab}\right)^{n}\left(\frac{a}{K_1}+\frac{a^n b}{K_2}\right)$$

This may be written :—

$$\log R_m=-n\log M_m+\log K_m \quad \text{(6)}$$

$$\text{where } K_m=\frac{(a+ab)^n}{\dfrac{a}{K_1}+\dfrac{a^n b}{K_2}}$$

(B) If the resistance of one constituent is very much higher than that of the other or, more precisely,

$$\text{if } \frac{b}{K_2}\left(\frac{aM_m}{a+ab}\right)^{n_2} \ll \frac{a}{K_1}\left(\frac{M_m}{a+ab}\right)^{n_1}$$

that is, if $F \ll 1$ where $F=\dfrac{bK_1}{aK_2}a^{n_2}\left(\dfrac{M_m}{a+ab}\right)^{n_2-n_1}$

we have $\log R_m \simeq -\log\dfrac{a}{K_1}\left(\dfrac{M_m}{a+ab}\right)^{n_1}$

This may be written :—

$$\log R_m=-n_1\log M_m+\log K_m \quad \text{(7)}$$

$$\text{where } K_m=\frac{K_1}{a}(a+ab)^{n_1}$$

EXPERIMENTAL

Experimental Details

The samples tested were prepared by the Spinning Department at the Shirley Institute. They consisted of three groups: (i) yarns of 6s count of pure cotton, pure wool and pure viscose staple, (ii) yarns of 6s count containing 25, 50 or 75 per cent of wool or viscose staple mixed with cotton early in the spinning process, and (iii) yarns of 24s/4 count made up from 1, 2 or 3 " singles " of wool or viscose staple, the remaining " singles " being cotton.

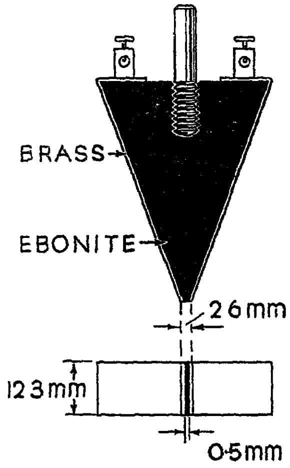


Fig. 1. Electrode System I

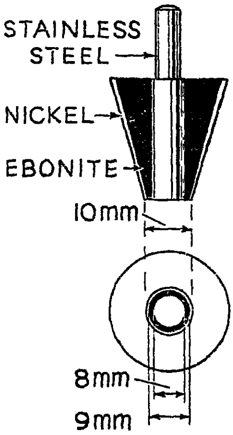
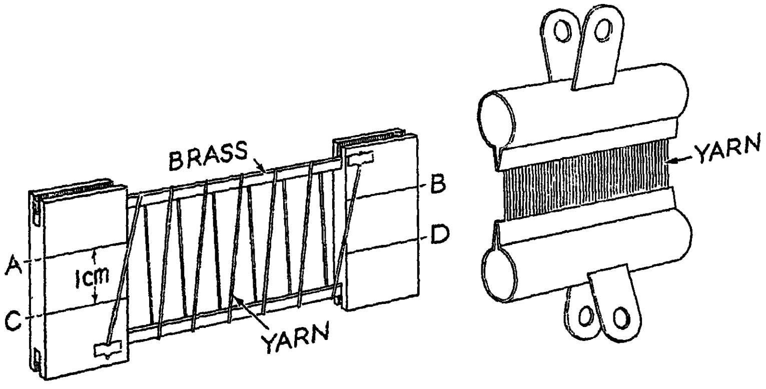


Fig. 2 Electrode System II



(a) (b)

Fig 3 Electrode System III

Two hanks of each sample, each containing about 10 gm, were placed in weighing bottles and partially dried by phosphorus pentoxide. They were then allowed to come into equilibrium by absorbing water from an atmosphere of constant R H. produced above a saturated salt solution in a closed vessel. The weight and electrical resistance of each sample were measured at this and successively higher humidities Finally, the samples were dried by standing them over phosphorus pentoxide until they lost no further weight. From the dry weight, and the previously found weights at each R.H., the moisture contents were calculated The losses of weight due to further drying in an oven were also found.

The resistances of the yarns across two different electrode systems were measured. Fig 1 shows the first electrode system which is in the form of a wedge ; it was fixed in the constant-pressure device designed for use with the Shirley Moisture Meter The hank of yarn was placed under the electrodes on an ebonite plate, so that the yarn lay horizontally and at right-angles to the gap between the electrodes ; the compressing force of 20 kgm. weight was applied and the resistance was measured on a Shirley Electrical Hygrometer, which had been specially calibrated against standard resistances. A temperature correction was applied to bring the reading to that which would have been indicated at 65° F. The second electrode system, conical in shape, is the " Raw Cotton Electrode " used with the Shirley Moisture Meter and shown in Fig. 2. The method of use was the same except that there was no need to align the yarn ; a Shirley Moisture Meter was used to measure the resistance

A third set of experiments was carried out by methods developed at the Shirley Institute by O'Sullivan About 50 turns of each yarn were wound on a former, as shown in Fig. 3 (*a*), and dried over anhydrous calcium chloride. Bulldog clips having edges covered with tin-foil were clipped along the lines AB and CD , when the former was removed the yarn was left hanging between the clips as in Fig. 3 (*b*). The clips were hung from insulated cup-hooks in a glass vessel containing a saturated salt solution giving a known R H. above it, and a fan to disturb the air The resistance was measured on the calibrated Shirley Electrical Hygrometer and was taken between the two cup-hooks without removing the sample from the vessel. The resistance was corrected for temperature and the value appropriate to 100 ends was calculated. Hanks, containing about 4 gm. each, were also hung in the vessel and, when the resistance had reached a steady value, taken out and weighed. The vessel was placed in an incubator at 20° C. till equilibrium had been eached. Further measurements were made at a greater R.H. The dry weight of the hanks was found by oven-drying and was corrected to the weight which would have been obtained if they had been dried by phosphorus pentoxide.

This last set of experiments gave the moisture contents at two values of R.H., but in further experiments to find moisture content at a given R H., a different method was used Hanks, containing about 10 gm. each, were placed in weighing bottles and dried over phosphorus pentoxide in a partial vacuum for several months. They were then weighed. They were allowed to absorb moisture by standing in a partial vacuum over saturated salt solutions giving successively higher relative humidities. When they had come into equilibrium at each R H , they were weighed and their moisture contents calculated

Effect of Electrode System

If the materials were homogeneous and isotropic and if their states (e.g., of compression) were not affected by the electrode system, the ratio of the resistances across two different electrode systems would be independent of the nature of the material and its moisture content , in other words, there would be a constant difference between the logarithms of their resistances That this does not apply to the resistance of yarn is shown by the variation in the differences of the logarithms given in Table I. It will be seen that the difference varies both with the nature of the material and with its moisture content The fairly small variations in the difference between the first and second electrode systems may be due to the difference in orientation of the yarn The variations in the difference between the first and third electrode systems may be due to the different pressure applied. The difference between the second and third electrode systems will combine both variations.

Table I
Effect of Different Electrode Systems

Sample	log M	Differences between values of log R for different electrode systems, i e log of ratio of resistances		
		I—II	I—III	II—III
Pure cotton	0·8	0·00	0·32	0·32
	1·0	0·27	0·19	—0·08
Pure wool	1·1	0·18	—0·48	—0·66
	1·3	0·03	—0·41	—0·44
Pure viscose staple	1·0	0·10	—0·31	—0·41
	1·2	0·24	—0·45	—0·69

Effect of Voltage

In the measurements made with the Electrical Hygrometer, the effect of varying the voltage from about 20 to 80 volts was investigated. In general it was found that the resistance was higher at a lower voltage, but some exceptions were found, and in no case was the difference much greater than the experimental error.

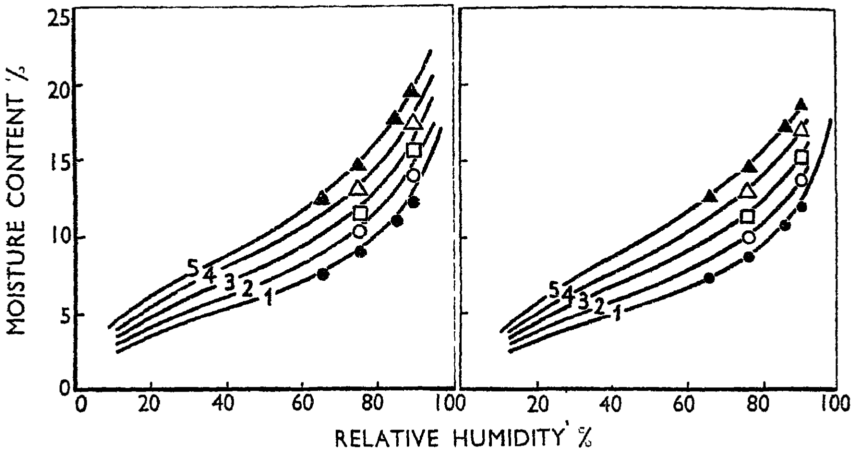


Fig 4

Curve 1. Pure cotton.
„ 2. 75% cotton, 25% viscose rayon
„ 3. 50% cotton, 50% viscose rayon
„ 4 25% cotton, 75% viscose rayon
„ 5 Pure viscose rayon.

The absorption curves for cotton and viscose rayon are extrapolated by using figures due to Urquhart.[6, 5] Curves 2, 3 and 4, are drawn by interpolation from curves 1 and 5. The plotted points represent experimental values

Fig. 5

Curve 1. Pure cotton.
„ 2 75% cotton, 25% wool
„ 3. 50% cotton, 50% wool.
„ 4 25% cotton, 75% wool.
„ 5. Pure wool.

The absorption curves for cotton and wool are extrapolated by using figures due to Urquhart[6] and Speakman[4] Curves 2, 3 and 4, are drawn by interpolation from curves 1 and 5. The plotted points represent experimental values.

Effect of Method of Mixing

For the cotton-viscose staple mixtures, there was no systematic difference between the resistances, at a given moisture content, of the yarn mixed in spinning and the yarn mixed by doubling.

For the cotton-wool mixtures, the resistance, at a given moisture content, of the doubled yarn was slightly greater than that of the yarn mixed in spinning. The difference was not great enough to be found accurately and no further account of it was taken.

Values of α

The values found for the moisture content of the yarns made from pure fibres after absorption to a known R.H. are given in Table II. From the figures of Urquhart and his collaborators for cotton[6] and viscose rayon[5] and Speakman's figures for wool,[4] particular samples were selected which fitted our values. These were used for extrapolation of the curves given in Figs 4 and 5, relating moisture content to R.H. From these curves values of α relative to cotton, were calculated and are plotted in Fig. 6.

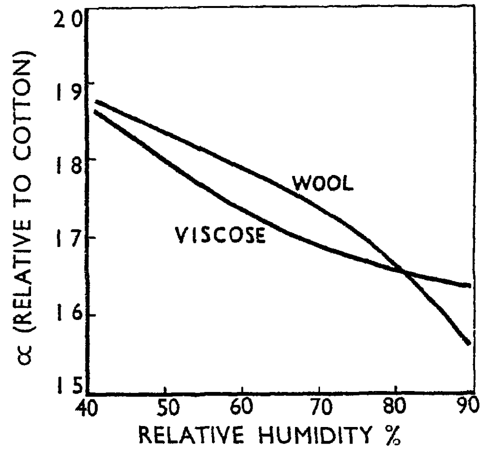


Fig 6.

Table II
Relative Humidity and Moisture Content

Saturated salt solution	Temp °C.	R.H. %	Sample	Moisture content %
Sodium nitrite	21	66	Cotton Viscose staple Wool	7·4 12·3 12·6
Sodium chloride	21	75	Cotton Viscose staple Wool	8·8 14·5 14·6
Sodium carbonate	21	86	Cotton Viscose staple Wool	10·8 17·6 17·3
Zinc sulphate	20	90	Cotton Viscose staple Wool	12·1 19·3 18·8

TESTING THE THEORETICAL EQUATIONS

We can now consider the application of the equations (5)-(7).

The values of n and log K for the pure materials for each electrode system are given in Table III. The experimental points and the lines from which n and log K were deduced are given in Figs. 7-12.

Table III
Values of n and log$K$

Sample	Electrode system					
	I		II		III	
	n	log K	n	log K	n	log K
Pure cotton	10·5	10·9	11·7	11·9	9·5	9·8
Pure viscose staple	10·5	13·4	11·7	14·6	9·5	12·8
Pure wool	15·9	21·4	15·2	20·4	17·7	23·9

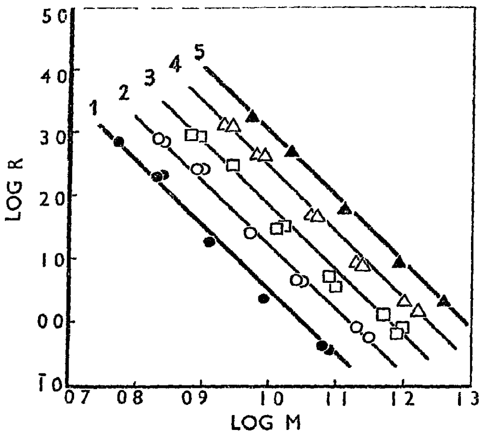


Fig. 7

Relation between the electrical resistance and the moisture content of cotton-viscose staple mixtures obtained by using electrode system I

Curve 1 Pure cotton from experimental points

Curve 2 Mixture 75% cotton, 25% viscose staple, deduced from equation (6)

Curve 3 Mixture 50% cotton, 50% viscose staple, deduced from equation (6).

Curve 4 Mixture 25% cotton, 75% viscose staple, deduced from equation (6).

Curve 5 Pure viscose staple from experimental points

All the plotted points represent the means of several experimental values

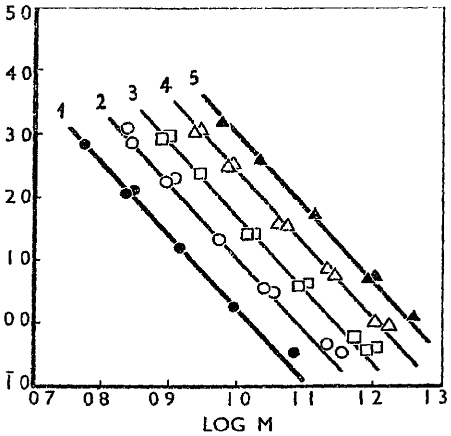


Fig. 8

Relation between the electrical resistance and the moisture content of cotton-viscose staple mixtures obtained by using electrode system II

Curve 1. Pure cotton from experimental points

Curve 2 Mixture 75% cotton, 25% viscose staple, deduced from equation (6).

Curve 3. Mixture 50% cotton, 50% viscose staple, deduced from equation (6)

Curve 4. Mixture 25% cotton, 75% viscose staple, deduced from equation (6)

Curve 5 Pure viscose staple from experimental points

All the plotted points represent the means of several experimental values

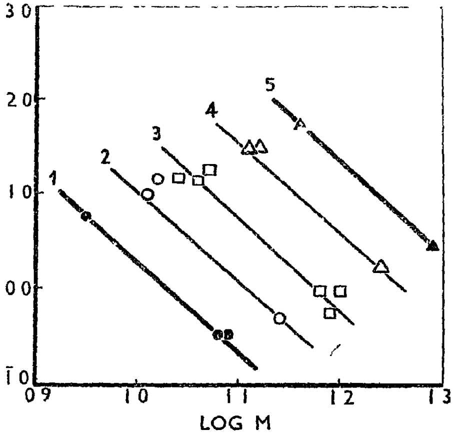


Fig 9

Relation between the electrical resistance and the moisture content of cotton-viscose staple mixtures obtained by using electrode system III

Curve 1. Pure cotton from experimental points.

Curve 2 Mixture 75% cotton, 25% viscose staple, deduced from equation (6)

Curve 3 Mixture 50% cotton, 50% viscose staple, deduced from equation (6).

Curve 4 Mixture 25% cotton, 75% viscose staple, deduced from equation (6).

Curve 5. Pure viscose staple from experimental points

All the plotted points represent the means of several experimental values

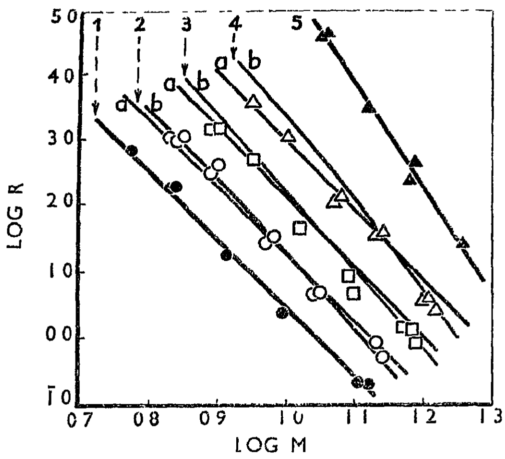


Fig 10

Relation between the electrical resistance and the moisture content of cotton-wool mixtures obtained by using electrode system I

Curve 1	Pure cotton from experimental points
Curve 2a	Mixture 75% cotton, 25% wool *
Curve 3a	Mixture 50% cotton, 50% wool *
Curve 4a	Mixture 25% cotton, 75% wool *
Curve 2b	Mixture 75% cotton, 25% wool †
Curve 3b	Mixture 50% cotton, 50% wool †
Curve 4b	Mixture 25% cotton, 75% wool †
Curve 5	Pure wool from experimental points

All the plotted points represent the means of several experimental values

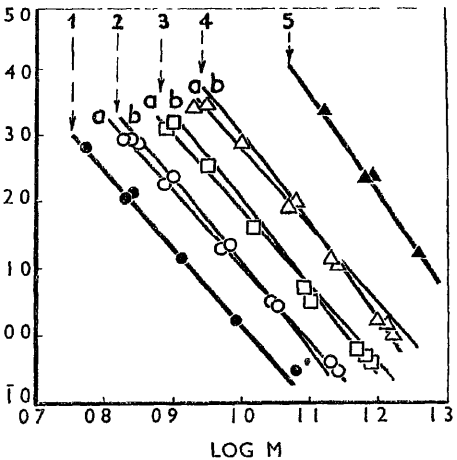


Fig 11

Relation between the electrical resistance and the moisture content of cotton-wool mixtures obtained by using electrode system II

Curve 1	Pure cotton from experimental points
Curve 2a	Mixture 75% cotton, 25% wool *
Curve 3a	Mixture 50% cotton, 50% wool *
Curve 4a	Mixture 25% cotton, 75% wool *
Curve 2b	Mixture 75% cotton, 25% wool †
Curve 3b	Mixture 50% cotton, 50% wool †
Curve 4b	Mixture 25% cotton, 75% wool †
Curve 5	Pure wool from experimental points

All the plotted points represent the means of several experimental values.

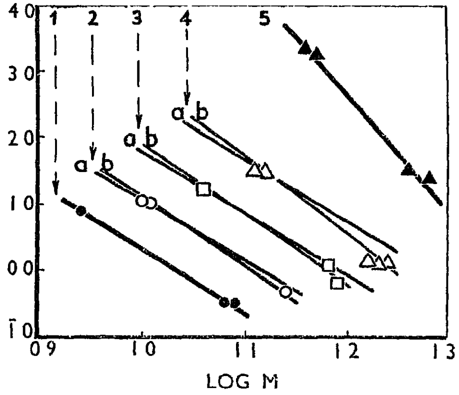


Fig. 12

Relation between the electrical resistance and the moisture content of cotton-wool mixtures obtained by using electrode system III.

Curve 1.	Pure cotton from experimental points.
Curve 2a	Mixture 75% cotton, 25% wool *
Curve 3a	Mixture 50% cotton, 50% wool *
Curve 4a	Mixture 25% cotton, 75% wool *
Curve 2b	Mixture 75% cotton, 25% wool †
Curve 3b	Mixture 50% cotton, 50% wool †
Curve 4b	Mixture 25% cotton, 75% wool †
Curve 5	Pure wool from experimental points

All the plotted points represent the means of several experimental values.

*From equation (7) taking $a=1{\cdot}70$ †From equation (7) using appropriate values of a.

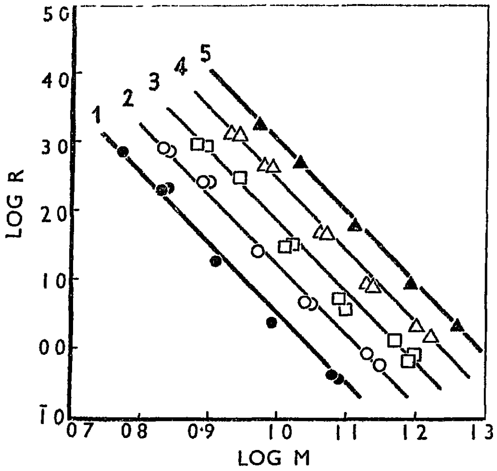


Fig 7

Relation between the electrical resistance and the moisture content of cotton-viscose staple mixtures obtained by using electrode system I

Curve 1 Pure cotton from experimental points

Curve 2 Mixture 75% cotton, 25% viscose staple, deduced from equation (6)

Curve 3 Mixture 50% cotton, 50% viscose staple, deduced from equation (6)

Curve 4 Mixture 25% cotton, 75% viscose staple, deduced from equation (6)

Curve 5 Pure viscose staple from experimental points.

All the plotted points represent the means of several experimental values

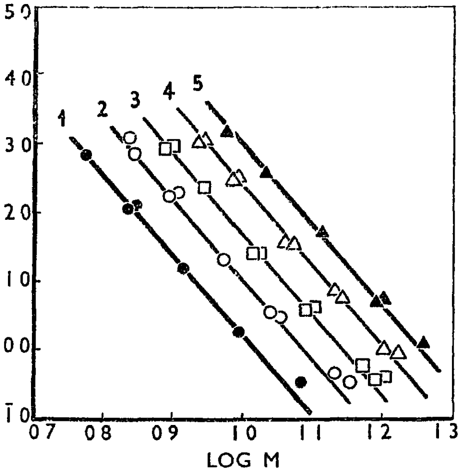


Fig. 8

Relation between the electrical resistance and the moisture content of cotton-viscose staple mixtures obtained by using electrode system II.

Curve 1. Pure cotton from experimental points

Curve 2 Mixture 75% cotton, 25% viscose staple, deduced from equation (6)

Curve 3 Mixture 50% cotton, 50% viscose staple, deduced from equation (6)

Curve 4 Mixture 25% cotton, 75% viscose staple, deduced from equation (6).

Curve 5. Pure viscose staple from experimental points

All the plotted points represent the means of several experimental values

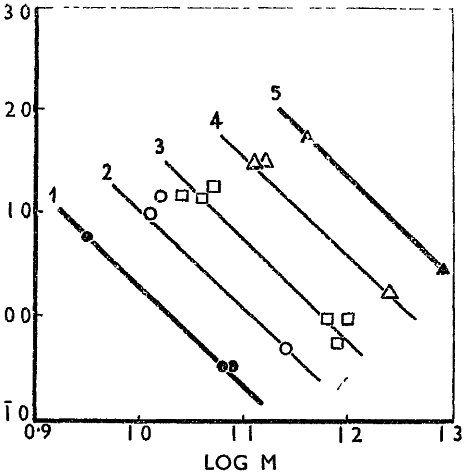


Fig. 9

Relation between the electrical resistance and the moisture content of cotton-viscose staple mixtures obtained by using electrode system III

Curve 1. Pure cotton from experimental points

Curve 2. Mixture 75% cotton, 25% viscose staple, deduced from equation (6)

Curve 3 Mixture 50% cotton, 50% viscose staple, deduced from equation (6).

Curve 4. Mixture 25% cotton, 75% viscose staple, deduced from equation (6).

Curve 5 Pure viscose staple from experimental points

All the plotted points represent the means of several experimental values

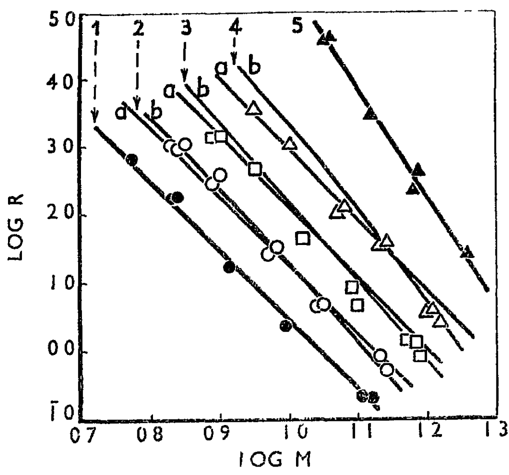


Fig 10

Relation between the electrical resistance and the moisture content of cotton-wool mixtures obtained by using electrode system I

Curve 1 Pure cotton from experimental points
Curve 2a Mixture 75% cotton, 25% wool *
Curve 3a Mixture 50% cotton, 50% wool *
Curve 4a Mixture 25% cotton, 75% wool *
Curve 2b. Mixture 75% cotton, 25% wool †
Curve 3b Mixture 50% cotton, 50% wool †
Curve 4b Mixture 25% cotton, 75% wool †
Curve 5 Pure wool from experimental points

All the plotted points represent the means of several experimental values

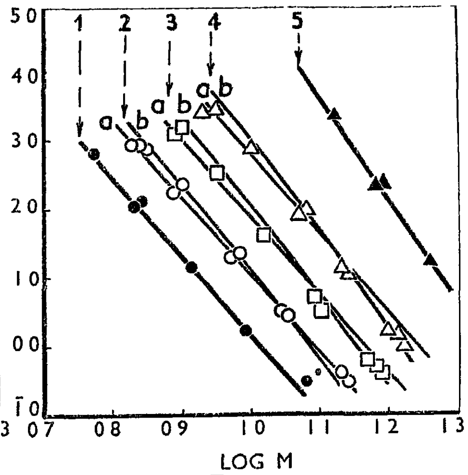


Fig 11

Relation between the electrical resistance and the moisture content of cotton-wool mixtures obtained by using electrode system II

Curve 1 Pure cotton from experimental points
Curve 2a Mixture 75% cotton, 25% wool *
Curve 3a Mixture 50% cotton, 50% wool *
Curve 4a Mixture 25% cotton, 75% wool *
Curve 2b Mixture 75% cotton, 25% wool †
Curve 3b Mixture 50% cotton, 50% wool †
Curve 4b Mixture 25% cotton, 75% wool †
Curve 5 Pure wool from experimental points

All the plotted points represent the means of several experimental values

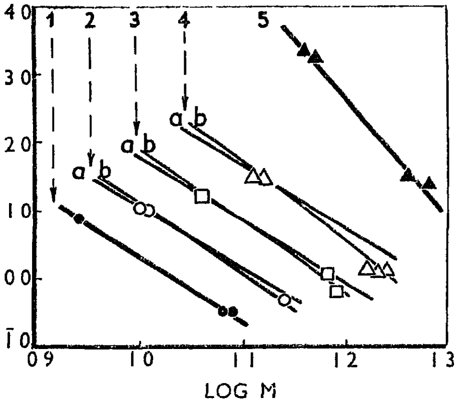


Fig 12

Relation between the electrical resistance and the moisture content of cotton-wool mixtures obtained by using electrode system III.

Curve 1 Pure cotton from experimental points
Curve 2a Mixture 75% cotton, 25% wool.*
Curve 3a. Mixture 50% cotton, 50% wool *
Curve 4a Mixture 25% cotton, 75% wool *
Curve 2b Mixture 75% cotton, 25% wool †
Curve 3b Mixture 50% cotton, 50% wool †
Curve 4b Mixture 25% cotton, 75% wool †
Curve 5. Pure wool from experimental points

All the plotted points represent the means of several experimental values.

*From equation (7) taking $a = 1{\cdot}70$ †From equation (7) using appropriate values of a

For mixtures of cotton and viscose staple special case (A) applies, since the values of n are the same, and we can test equation (6). Table IV gives values of log K_m obtained when a constant value of α equal to 1·70 was used. The lines derived from these values are given in Figs 7, 8 and 9, the experimental points are plotted for comparison. The figures given in Table V show that the error introduced by using a constant value of α is negligible.

Table IV

Values of logK_m, in Equation (6) for Viscose Staple Mixtures and in Equation (7) for Wool Mixtures, putting $\alpha = 1.70$ in both Equations

Sample	Electrode system			Sample	Electrode system		
	I	II	III		I	II	III
75% Cotton 25% Viscose staple	11·65	12·72	10·6	75% Cotton 25% Wool	11·77	12·83	10·6
50% Cotton 50% Viscose staple	12·23	13·41	11·2	50% Cotton 50% Wool	12·55	13·71	11·3
25% Cotton 75% Viscose staple	12·87	14·06	12·0	25% Cotton 75% Wool	13·40	14·63	12·1

Table V

Effect of α on Values of logK_m for Cotton-Viscose Staple Mixtures

a (Cotton)	b (Viscose staple)	α (Relative to cotton)	log K_m			Difference of value of log K_m from value of log K at $\alpha = 1.70$		
			Electrode system			Electrode system		
			I	II	III	I	II	III
0·75	0·25	1·80	11·68	12·74	10·68	0·03	0·02	0·12
0·75	0·25	1·70	11·65	12·72	10·56	—	—	—
0·75	0·25	1·64	11·63	12·69	10·52	0·02	0·03	0·04
0·25	0·75	1·80	12·90	14·10	12·09	0·03	0·04	0·11
0·25	0·75	1·70	12·87	14·06	11·98	—	—	—

For cotton-wool mixtures the values of F* are given in Table VI. Except for mixtures containing much wool at a high moisture content we see that $F \leqslant 1$ and so special case (B) applies. In Figs 10, 11 and 12, the curves derived from equation (7) and appropriate values of α are compared with the experimental results and with the lines obtained by substituting in equation (7) the values of log K_m given in Table IV, which were calculated for a constant value of α equal to 1·70.

Table VI

Values of F for Cotton and Wool, taking $\alpha = 1.70$

a (Cotton)	b (Wool)	Moisture content %	F
0·75	0·25	16	0·06
0·50	0·50	16	0·09
0·25	0·75	16	0·14
0·25	0·75	13	0·04

In all cases the experimental results support the equations which were derived from the assumptions given earlier in this paper

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* See Case (B) under "*Equations to be Tested*"

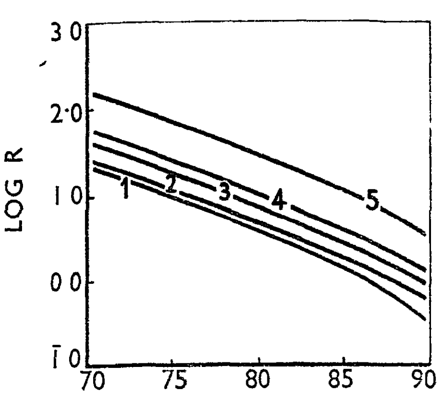

Fig. 13

Relation between the electrical resistance and the equilibrium relative humidity of cotton-viscose staple mixtures obtained by using electrode system III.

Curve 1 Pure cotton
„ 2 75% cotton, 25% viscose staple.
„ 3 50% cotton, 50% viscose staple
„ 4 25% cotton, 75% viscose staple
„ 5 Pure viscose staple

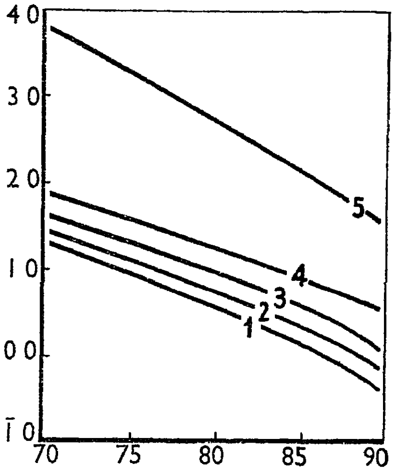

Fig. 14

Relation between the electrical resistance and the equilibrium relative humidity of cotton-wool mixtures, obtained by using electrode system III.

Curve 1 Pure cotton
„ 2 75% cotton, 25% wool
„ 3 50% cotton, 50% wool.
„ 4. 25% cotton, 75% wool.
„ 5 Pure wool

RELATION OF THE RESISTANCE TO THE RELATIVE HUMIDITY OF THE YARN

For some purposes it is more convenient to consider the Relative Humidity of the atmosphere with which the yarn is in equilibrium (briefly described as the " R H. of the yarn ") instead of the moisture content of the yarn. The curves relating R H. to moisture content for the yarns of pure fibres were obtained as explained earlier and are given in Figs 4 and 5. By interpolation, using equation (3), the curves for the mixed yarns were found and are included in Figs 4 and 5 From these curves and from the lines in Figs 9 and 12 relating log R to log M, the curves given in Figs 13 and 14, relating R.H. to log R for electrode system III, were deduced The curves for cotton* show good agreement with the formula for the Electrical Hygrometer, given in the introduction :—

$$\log R = 8{\cdot}1 - \log\frac{E}{NL} - 0{\cdot}0715\,H.$$

This equation is of the same form as that given by Walker[7] for cotton at high humidities.

PRACTICAL APPLICATIONS

The use of equation (5), or a simplified form of it, enables a calculation to be made of the moisture content of a yarn containing known amounts of two fibres, if its resistance and certain properties of the yarns of the pure fibres are known. This equation has been confirmed by the present experiments and there is no reason to suppose that its application is not more general. It can easily be extended to a yarn containing more than two fibres; the general equation for a yarn containing z sorts of fibres, derived by a method similar to that for a two-fold mixture, is :—

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* The difference between cotton and viscose staple is greater than that previously found A full explanation of this apparent discrepancy is given in the Appendix

$$\log R_m = -\log\left\{\sum_{r=1}^{r=z}\frac{a_r}{K_r}\left(\frac{\alpha_r M_m}{\sum\limits_{\rho=1}^{\rho=z} a_\rho \alpha_\rho}\right)^{n_r}\right\}$$

To apply these results for wool and viscose staple mixed with cotton to the Shirley Moisture Meter it is convenient to use equations (6) and (7), which may both be written :—

$$\log R_m = -n_1 \log M_m + \log K_m$$

though the expressions for K_m differ in the two equations. For pure cotton :—

$$\log R_1 = -n_1 \log M_1 + \log K_1$$

If M'_1 is the moisture content deduced from the Moisture Meter reading (taking account of the electrode system used and of the fact that the Moisture Meter is calibrated in moisture regain) on the assumption that the yarn is pure cotton then :—

$$-n_1 \log M_m + \log K_m = -n_1 \log M'_1 + \log K_1$$

$$\therefore\ M_m = M'_1 \left(\frac{K_m}{K_1}\right)^{\frac{1}{n_1}}$$

Thus conversion factors can be calculated for the various mixed yarns.

If the curves relating log R to R.H for any material or mixture are straight lines parallel to the line for cotton, the Electrical Hygrometer calibration will be correct if the warp factor is multiplied by the antilog of the difference in log R between the cotton line and the line for the other material or mixture. If the slopes are different a conversion factor of this type can be used to make the mid-scale reading correct, but the calibration on the dial will also have to be corrected.

APPENDIX

Comparison between the Resistance of Viscose Staple Yarn and Cotton Yarn at the same Relative Humidity.

Introduction

Previous experiments made at the Shirley Institute indicated that the difference between the values of log R for cotton yarn and for viscose staple yarn, at the same relative humidity, was about 0·3, leading to the use with the Electrical Hygrometer of a corrected warp factor of $\frac{1}{2} \times E/N$. But the results given in Fig. 13 indicate that the difference is 0·9 The following series of experiments was designed to investigate the reason for this disagreement

Experimental Details

A range of samples of "Fibro"* was obtained and also some samples of cotton to be used as standards. The complete list of samples is given in Tables VII and VIII Half of each sample was sized on the model tape-frame[1] at the Shirley Institute with size mixings consisting of maize starch and a small percentage of tallow. The viscose staple was sized to a nominal 7 per cent. and the cotton to a nominal 12 per cent., both expressed as a percentage of the weight of unsized material.

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* Viscose staple yarn made by Messrs Courtaulds, Ltd.

Table IX

Values of log*R* for Samples Conditioned at 25°C. (approx.)

(The letter S before a sample indicates that it is a sized sample)

Set 1 Approx. 65% R H	Sample	6	7	8	10	16	S7	S8	12	13	14	15	S12
Saturated NaNO$_2$ solution	log *R*	1·77	1·58	1·56	1·46	1·66	1·48	1·46	1·29	1·33	1·46	1·22	1·32
Set 2 Ditto	Sample	3	8	9	17	18	S3	S8	S9	S18	12	S12	S13
	log *R*	1·70	1·74	1·80	1·68	1·64	1·48	1·63	1·47	1·45	1·39	1·47	1·19
Set 3 Ditto	Sample	1	2	4	8	11	S1	S2	S4	S8	S11	12	S12
	log *R*	1·89	1·87	1·57	1·99	1·86	1·64	1·63	1·56	1·76	1·79	1·49	1·69
Set 4 Ditto	Sample	S4	S5	S6	S8	S10	S16	S17	S19	S12	S13	S14	S15
	log *R*	1·94	2·21	2·46	2·49	2·45	2·52	2·35	2·36	2·26	2·05	2·01	1·75
Set 5 Ditto	Sample	4	5	6	8	10	16	17	19	12	13	14	15
	log *R*	2·37	2·44	2·49	2·44	2·39	2·64	2·44	2·44	1·84	1·82	2·06	1·79
Set 8 Approx 43% R H	Sample	2	5	16	18	S5	S16	S18	12	13	15		S15
Saturated K$_2$CO$_3$ solution	log *R*	3·76	3·77	3·85	3·93	3·85	3·84	3·93	3·41	3·42	3·30		3·46
Set 9 Approx 65% R H	Sample	2	5	16	18	S5	S16	S18	12	13	15		S15
Saturated NaNO$_2$ solution	log *R*	2·55	2·53	2·67	2·55	2·39	2·46	2·50	2·03	1·93	1·98		2·01
Set 10 Approx 75% R H	Sample	2	5	16	18	S5	S16		12	13	15		S15
Saturated NaCl solution	log *R*	1·67	1·66	1·98	1·78	1·61	1·77		1·16	1·00	1·11		1·09
Set 11 Approx 85% R H.	Sample	2	5	16	18	S5	S16	S18	12	13	15		S15
Saturated KCl solution	log *R*	0·81	0·83	1·19	1·00	0·85	1·02	1·03	0·30	0·12	0·29		0·36

Table X

Values of log (R_v/R_{sv}) for Samples Conditioned Together

Sample No	1	2	3	4	5	7	8
Set No	3	3	2	3	9	1	1
log (R_v/R_{sv})	0·25	0·24	0·22	0·01	0·14	0·10	0·10
Sample No	8	8	9	11	16	18	18
Set No	2	3	2	3	9	2	9
log (R_v/R_{sv})	0·11	0·23	0·32	0·07	0·21	0·21	0·05

(*b*) *Difference between cotton and unsized viscose staple at approximately* 65 *per cent. R.H. and* 25° *C.*

Table XI gives the value of $\log(R_v/R_c)$ for each set. Combining the results for all the sets we have —

$$\text{Weighted mean } \log(R_v/R_c) = 0{\cdot}44$$

where the weight given to the value for any set is equal to the product of the numbers of samples of cotton and of unsized viscose staple in that set.

Table XI

Values of log (R_v/R_c) at about 65% R.H. and 25°C.

Set	No. of cotton samples	Mean log R for cotton	No of unsized viscose samples	Mean log R for unsized viscose	log (R_v/R_c)	Weight
1	5	1·32±0·08*	5	1·61±0·10*	0·29	25
2	3	1·35±0·12	5	1·71±0·05	0·36	15
3	2	1·59±0·10	5	1·83±0·14	0·24	10
5	4	1·88±0·10	8	2·46±0·08	0·58	32
9	4	1·99±0·04	4	2·57±0·06	0·58	16

* Standard deviation.

(*c*) *Difference between cotton and sized viscose staple at approximately* 65 *per cent. R H. and* 25° *C.*

Table XII gives the values of $\log(R_{sv}/R_c)$. Combining the results in the same way as above, we have —

$$\text{Weighted mean } \log(R_{sv}/R_c) = 0{\cdot}27.$$

Table XII

Values of log (R_{sv}/R_c) at about 65% R.H. and 25°C.

Set	No of cotton samples	Mean log R for cotton	No of sized viscose samples	Mean log R for sized viscose	log (R_{sv}/R_c)	Weight
1	5	1·32±0·08*	2	1·47±0·01*	0·15	10
2	3	1·35±0·12	4	1·51±0·07	0·16	12
3	2	1·59±0·10	5	1·67±0·09	0·08	10
4	4	2·02±0·18	8	2·35±0·18	0·33	32
9	4	1·99±0·04	3	2·44±0·05	0·45	12

* Standard deviation

(*d*) *Variation with humidity at* 25° *C*

Sets 8, 9, 10 and 11 are for the same samples over a range of humidities from approximately 43 per cent to approximately 85 per cent R.H The results indicate that at either end of this range the difference between sized and unsized viscose staple becomes less pronounced

Table XIII gives the values of $\log(R_v/R_c)$ and of $\log(R_{sv}/R_c)$ for this range of humidities It will be seen that the difference between cotton and viscose staple becomes much greater at high humidities.

Table XIII
Values of log (R_v/R_c) and log (R_{sv}/R_c) at 25°C. and various humidities

Set	R.H.% approx.	Mean log R for cotton	Mean log R for unsized viscose	Mean log R for sized viscose	log (R_v/R_c)	log (R_{sv}/R_c)
8	43	3·40±0·06*	3·83±0·05*	3·87±0·04*	0·43	0·47
9	65	1·99±0·04	2·57±0·06	2·44±0·05	0·58	0·45
10	75	1·08±0·06	1·76±0·13	1·69±0·08	0·68	0·61
11	85	0·27±0·09	0·96±0·15	0·97±0·08	0·69	0·70

* Standard deviation

Conclusion

The value of log(R_v/R_c) of about 0·9 given by the results in Fig. 13 is due to the high humidity at which these measurements were made. At relative humidities of about 65 per cent. the value of log(R_{sv}/R_c) is about 0·3 and thus, when viscose staple yarns are being measured by an Electrical Hygrometer calibrated in equilibrium R.H. for cotton yarns, the division of the warp factor by 2 (the antilog. of 0·3) is a suitable correction.

ACKNOWLEDGEMENT

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REFERENCES

[1] Farrow, F. D., and Jones, E. H. *Shirley Inst. Mem.*, 1926, 5, 275; or *J. Text. Inst.*, 1927, 18, T1.

[2] Jones, E. H. *J. Sci. Instruments*, 1940, 17, 55.

[3] Murphy, E. J., and Walker, A. C. *J. Phys. Chem.*, 1928, 32, 1761.

[4] Speakman, J. B. *J. Soc. Chem. Ind.*, 1930, 49, 210T.

[5] Urquhart, A. R., and Eckersall, N. *Shirley Inst. Mem.*, 1932, 11, 75; or *J. Text. Inst.*, 1932, 23, T163.

[6] Urquhart, A. R., and Williams, A. M. *Shirley Inst. Mem.*, 1924, 3, 49; or *J. Text. Inst.*, 1924, 15, T138.

[7] Walker, A. C. *J. Text. Inst.*, 1933, 24, T145.

[8] Walker, A. C. *Textile Research*, 1937, 7, 289.

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19—VISCOSE RAYON FIBRES
II—THE ORIENTATIONS OF SKIN AND CORE

By J. M Preston and K. I. Narasimhan

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INTRODUCTION

In the previous communication[1] it was shown that the fibre refractometer[2] measures the refractive indices of the core of viscose fibres. It is well known that the Becke method[3] measures the refractive indices of the skin of fibres.[4] It follows that measurements on the same fibres by the two methods should give a rapid and simple way of measuring the optical properties and through them the orientations of skin and core. Wuhrmann[4] used a beautiful but difficult microscopical technique to measure the difference between the double refractions of skin and core and with it obtained data for six commercial viscose fibres. These data confirmed that the skin had a higher axial orientation than the core in every case as had been previously deduced from other observations.[5,6] Wuhrmann's measurements covered only a small range of fibres and were made on viscoses of unstated commercial manufacture. A large range of fibres of known methods of manufacture must be examined to find any systematic relationship. It was believed that if this were done it would help to elucidate further the structures of the skin and core of viscose fibres. The conjoined use of the Becke and fibre refractometer methods appeared to offer a comparatively simple technique for the purpose. It was decided to examine several series of specially prepared fibres by the new combination of techniques.

EXPERIMENTAL

Several series of viscose fibres were spun by the methods described previously.[7,8] In each series, fibres with a range of orientations were spun. The results for three series of these specially prepared fibres are given in the present communication. The fibres range from comparatively homogeneous ones spun into ammonium sulphate baths to fibres with well defined skins spun into baths containing the sulphates of zinc and sodium and sulphuric acid. Data for a commercial cuprammonium fibre are also included. The experimental fibres were all desulphurized, dried and conditioned at 65 per cent. R.H.

Table I

Viscose Fibres, Series A

(Spun into approximately neutral 55% ammonium sulphate at 45° C)

Filament denier	Refractive indices			
	Core		Skin	
	$n_{\parallel}$	$n_{\perp}$	$n_{\parallel}$	$n_{\perp}$
4·5	1·5400	1·5173	1·5440	1·5185
,,	1·5404	1·5170	1·5446	1·5184
,,	1·5430	1·5162	1·5486	1·5164
,,	1·5438	1·5159	1·5502	1·5162
,,	1·5477	1·5150	1·5550	1·5136
,,	1·5389	1·5161	1·5416	1·5185
,,	1·5399	1·5160	1·5434	1·5177
,,	1·5422	1·5150	1·5480	1·5168
,,	1·5442	1·5148	1·5512	1·5160
,,	1·5465	1·5143	1·5545	1·5151
,,	1·5400	1·5176	1·5435	1·5199
—	1·5300	1·5281	1·5296	1·5288

The refractive index measurements were made in methyl salicylate, ethyl salicylate, nitrobenzene and anisole which had been conditioned at 65 per cent. R.H. The fibre refractometer was used in the way previously described.[2] The Becke method was used in the usual way.[3] In order to reach equivalence of refractive indices between fibres and immersion liquid in the Becke method, the wave length of the illuminating light was varied till the Becke line disappeared. The refractive indices were converted to the values at the D line by the method described for the fibre refractometer [2]

Viscose Fibres, Series B

(Spun into a solution of 20% sodium sulphate and 12% sulphuric acid at 45°C)

Filament denier	Refractive indices			
	Core		Skin	
	$n_{\parallel}$	$n_{\perp}$	$n_{\parallel}$	$n_{\perp}$
4·5	1·5379	1·5184	1·5415	1·5173
,,	1·5341	1·5165	1·5412	1·5173
,,	1·5393	1·5160	1·5443	1·5166
,,	1·5391	1·5155	1·5455	1·5160
,,	1·5416	1·5149	1·5475	1·5145
,,	1·5309	1·5155	1·5365	1·5159

Cuprammonium Rayon Fibres

Filament denier	Refractive indices			
	Core		Skin	
	$n_{\parallel}$	$n_{\perp}$	$n_{\parallel}$	$n_{\perp}$
—	1·5471	1·5185	1·5521	1·5199

Viscose Fibres, Series C

(Spun into a solution of 20% sodium sulphate, 2% zinc sulphate and 12% sulphuric acid at 45° C)

Filament denier	Refractive indices			
	Core		Skin	
	$n_{\parallel}$	$n_{\perp}$	$n_{\parallel}$	$n_{\perp}$
6·5	1·5382	1·5184	1·5457	1·5173
,,	1·5384	1·5184	1·5461	1·5172
4·5	1·5370	1·5151	1·5443	1·5162
,,	1·5378	1·5150	1·5468	1·5155
,,	1·5389	1·5155	1·5479	1·5163
,,	1·5399	1·5148	1·5492	1·5158
,,	1·5412	1·5146	1·5502	1·5153
,,	1·5414	1·5146	1·5507	1·5151
,,	1·5427	1·5137	1·5523	1·5145
,,	1·5289	1·5186	1·5350	1·5179
,,	1·5313	1·5178	1·5371	1·5164
,,	1·5346	1·5173	1·5394	1·5169
,,	1·5349	1·5168	1·5409	1·5162
,,	1·5368	1·5163	1·5427	1·5152
,,	1·5283	1·5211	1·5302	1·5212
,,	1·5293	1·5208	1·5321	1·5206
,,	1·5294	1·5200	1·5334	1·5199
,,	1·5249	1·5197	1·5317	1·5228
,,	1·5325	1·5207	1·5370	1·5203
,,	1·5332	1·5203	1·5384	1·5198
,,	1·5316	1·5211	1·5356	1·5206
,,	1·5287	1·5210	1·5310	1·5208

The data for the refractive indices of the skin and core of the different fibres are given in Table I The double refractions of the core and skin in each case are plotted as ordinates and abscissæ, respectively, in Fig. 1. The different sets of data from the different series of viscose fibres all show similar and nearly parallel trends. Although the sets of points lie fairly close together the sets clearly do not overlap, but lie along distinct lines. For all except the point representing the nearly isotropic fibres the skin double refraction, is greater than the core double refraction This difference is greatest for the fibres spun into the zinc sulphate bath, next greatest for the fibres spun into the acid sodium sulphate bath Next stand the fibres spun into the ammonium sulphate bath, and last of all the fibres with the least difference, the commercial cuprammonium fibres.

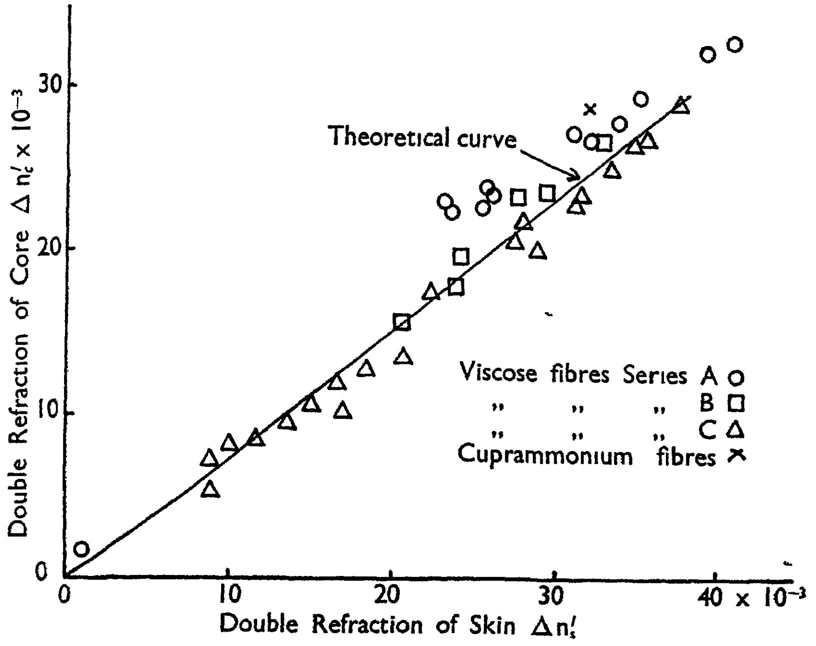

Fig. 1.

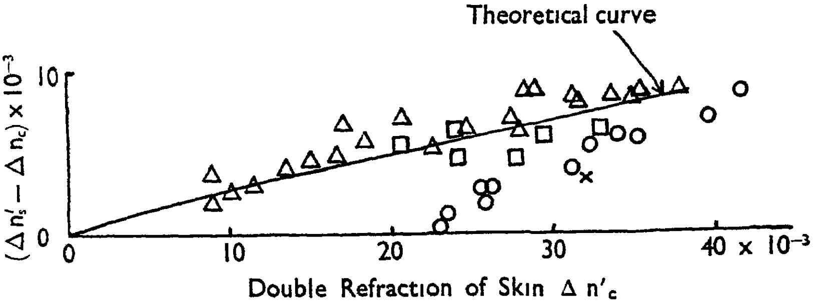

Fig 2.

DISCUSSION

It is clear from the trends of the experimental points in Fig 1 that the double refractions of skin and core are symbatic. It is also clear from the general trend of all the data that the double refraction of the skin increases faster than that of the core These relations are exhibited more clearly if the difference between the double refractions of skin and core is plotted against the double refraction of the skin for each fibre This plot has been made in Fig. 2. In this figure it is seen in each of the three series of fibres that the difference between the double refractions increases with increase of double refraction. It is also seen that the difference between skin and core is greatest for the fibres spun into the zinc sulphate containing bath. The fibres spun into the acid sodium sulphate bath, as might be expected, occupy an intermediate position. The low single value for cuprammonium rayon indicates the *comparative* absence of a more oriented skin for these fibres.

The experimental points of Fig. 2 show that the orientations of skin and core are nearly the same when both are small, but that as the fibres are stretched in spinning the orientation of the skin increases faster than that of the core. The results of Fig. 2 also show that the fibres with the most pronounced skins, those spun into a bath containing zinc sulphate, show the differential effect of stretch most markedly. The fibres which are usually considered skinless or have scarcely detectable skins show the differential effect of stretching least on the double refractions of skin and core. This is seen in the data for the cuprammonium fibres and the viscose fibres spun into ammonium sulphate* baths. The angle at which the line of points for the fibres spun into the ammonium sulphate meets the axis in Fig. 2 suggests that the difference might become negative for less oriented fibres. The suggestion is supported by the single value for nearly isotropic fibres shown in Fig. 1. The data for these fibres show that their cores are more oriented than their skins. It will be necessary to spin fibres of intermediate orientations to test the suggested course of the curve.

The fibres spun into baths containing zinc sulphate have highly serrated cross sections. Their peripheries have serration coefficients of about 1·6.[7] The fibres spun into the ammonium sulphate bath have nearly circular cross sections and serration coefficients near to unity. Hermans has shown[9] that the skin of serrated viscose fibres exhibits negative double refraction in the tangential direction or what is the same thing positive double refraction in the normal or radial direction. This is a most significant observation when considered in conjunction with Sisson's important observations on the orienting effect of shrinkage.[10] The two sets of observations taken together point clearly to the presence of a radial uniplanar orientation of the cellulose in the skin. Sisson writing earlier† and therefore without knowledge of the phenomena just reported by Hermans had suggested that there was a tangential uniplanar orientation of the skin [11] He had based this on the axial orientation of the 101 planes shown by his X-ray diagrams and the fact that the cross sections of viscose fibres contract during spinning. The X-ray diagram produced when a whole fibre or bundle of fibres is irradiated does not distinguish between the tangential orientation suggested by Sisson and the radial orientation suggested here. This is clear from Figs. 3a and 3b. Fig. 3a shows the suggested tangential and Fig. 3b. the suggested radial

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*The new staining technique of P. H Hermans (*Text Res. J*, 1948, 18, 9) indicates the presence of a thin skin even with these fibres

†Similarly, Horio, Kobayashi and Kondo (*Text Res. J*, 1947, 17, 264) published their interpretation of their electron microscopic observations before Hermans' work. They observed elliptical bubbles which they suggest are evidence of compression during coagulation. The shape of these bubbles could equally have resulted from compression by the knife during section cutting Support is lent to the latter explanation since the ellipses lie with their short axes in the direction of cutting, which can be seen from the knife scratches on the sections

uniplanar orientations It is clear that the 101 planes lie parallel to the fibre axis and at all orientations in the plane perpendicular to the fibre axis in both cases The idea of a radial orientation is more consistent with Sisson's observations on shrinkage than is the idea of a tangential orientation of the skin. This will be seen when the method of fibre formation is considered in detail The important point to consider is the serrated shape of cross sections of fibres with marked skins This comes from the lateral compression of the skin during the shrinkage of the core, as the folds form in any flexible but more or less incompressible structure which is pressed together The fibres are restrained mechanically from shrinking axially so that most if not all of the shrinkage is *transverse.* Thus in the skin the transverse tangential shrinkage orients the cellulose chains more or less completely in radial planes normal to the fibre surface The orientation in these planes is only partially complete, as can be deduced from the quantitative data, but it is sufficiently marked to account for many otherwise inexplicable properties of the fibres.

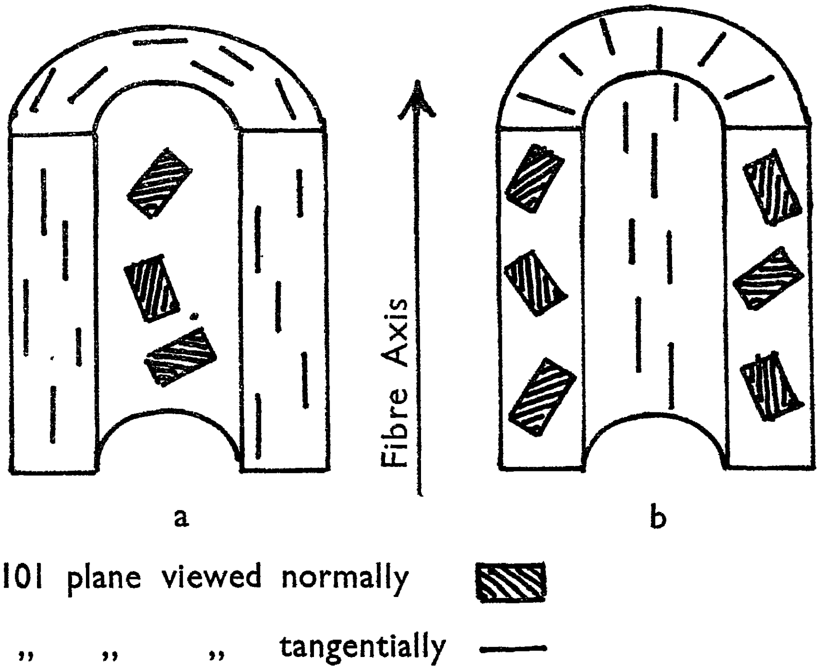

Fig 3

To test the radial structure hypothesis it is necessary to see how far it fits in with other known facts. One fact is that the skin is denser and swells less than the core.[12,13] This appears reasonable when it is considered that the skin is in compression, whilst the core is in tension due to the osmotic action of the coagulating bath during formation of the filaments These conditions would be expected to produce a more compact structure in the skin than in the core Another observation, reported by Hermans[9], which must be considered is that the magnitude of the transverse double refraction of the skin decreases with increase of stretch. If there is in fact a radial orientation of the cellulose chains in the skin, then the double transverse refraction must be a function of the axial orientation as well. Since it has been reported[14] that there is little difference between the two transverse refractive indices n_α and n_β it follows that a perfect axial orientation will have a very small transverse double refraction. On the other hand a poor axial orientation combined with a good radial one will exhibit a high double transverse refraction. It follows that increase of stretch should decrease the transverse double refraction as is found experimentally.

A higher rate of increase of orientation with stretch of the 101 compared to the $10\bar{1}$ and 002 planes is reported by Hermans[15] for ordinary viscose (which has a skin) but not for Lilienfeld viscose, which is said to be without a skin.[16] The axial orientation of the 101 planes, already partially oriented by shrinkage, would, when stretch is applied, be expected to proceed more rapidly than the orientation of the other planes which have a spatially random disposition. Another effect of stretch which operates in the same direction should be mentioned. Stretch as usually applied does not alter the initial and final speeds of the fibre being spun. It alters the position at which the fibre is attenuated as shown diagrammatically in Fig. 4. The more the stretch the less is the attenuation in the coagulating bath at the spinneret. A less attenuated fibre will have a greater periphery and thus the skin will have a greater area and will be subjected to more transverse compression to accommodate itself to the final attenuated volume. The greater transverse compression of the skin of stretched fibres should result in a greater orientation of the 101 planes. This agrees with the experimental evidence.

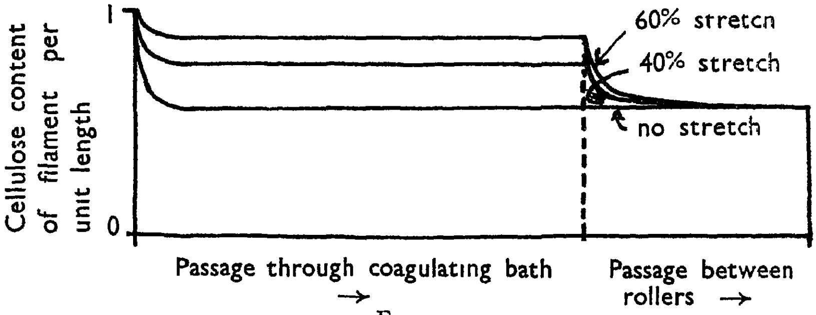
Cellulose content of filament per unit length
1
0
60% stretch
40% stretch
no stretch
Passage through coagulating bath →
Passage between rollers →

Fig 4

Schematic Representation of the Attenuation of Filaments during the Spinning of Viscose

Another observation that must be fitted into any picture of the structures of skin and core is the one exception noted by Rose[17] to his interesting correlation of double refraction with the slope of the load-elongation curves of viscose fibres. The one exception is Bemberg cuprammonium fibre. From the slope of the load-elongation curve the double refraction would be expected to be about 0·022, whereas the value found experimentally is 0·0302. The explanation appears to be that the double refractions were measured on the cores of the fibres whilst the slope of the load-elongation curve in the region used depends on the skin, according to Wuhrmann.[18] Now except for a few unstretched fibres all Rose's fibres were spun into baths containing zinc sulphate. Fig. 1 shows that these fibres have a nearly linear relation between the double refractions of skin and core. The effect of substituting measurements of skin and core for one another therefore effectively introduces a constant multiplying factor which can be neglected unless fibres of a different kind are considered. Cuprammonium fibres are of a different kind structurally. They possess comparatively poorly oriented skins which are so thin that they are not observable under the microscope by the usual technique. It may be considered that when stretching these fibres the load is borne by the core. In this case when using Rose's correlation factor the equivalent double refraction is that of the core of a viscose fibre with the skin orientation equivalent to that measured for the core of the cuprammonium fibre From the curve for zinc sulphate viscose fibres in Fig 2 the difference in orientation between the skin and core of such a fibre is about 0·008 If this is subtracted from the measured value 0·0302 it brings it to the expected value 0·0222.

As all the tests known to us that could be applied to the hypothesis led to deductions which were consistent with the proposed skin and core structures it was decided to attempt to devise a theoretical quantitative relation between the skin and the core structures As far as is known to us this has not been done before It is put forward as a first approach to the solution of the problem without any attempt at refinement because it was felt that at this stage it would be inappropriate to use any but the simplest treatment

From the preceding discussion it will have been seen that the hypothesis proposed to give a rational picture of the properties of the skin and core is that there are two kinds of structure present The skin is considered to have a partially planar structure oriented in the radial direction The core is considered to have the usually assumed spatial structure Hermans[10] has derived a simple relation between the double refraction and the mean angle of a uniaxial spatial structure. It is:

$$\frac{\Delta n_c}{\Delta n_o} = 1 - 3/2 \sin^2\phi \qquad \text{. . . . . . . (i)}$$

where Δn_c and Δn_o are the double refractions of the actual fibre and of a perfectly oriented fibre The mean angle of the fibre structure is ϕ.

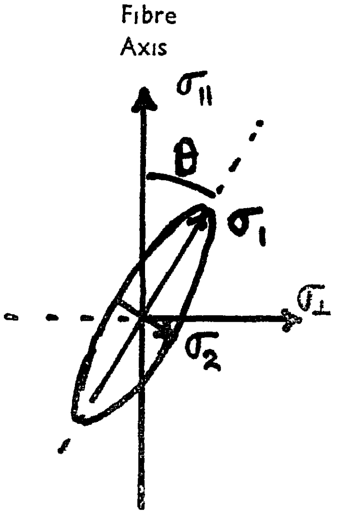

Fig. 5.

A similar relation can be derived for a planar structure Thus if Fig 5 represents a cellulose chain or crystallite lying in the plane of the paper and at an angle θ to the fibre axis then if $\sigma_{\parallel}$, $\sigma_{\perp}$, σ_1 and σ_2 are the polarizabilities

$$\sigma_{\parallel} = \sigma_1 \cos^2\theta + \sigma_2 \sin^2\theta \qquad \text{(ii)}$$

$$\begin{aligned}\sigma_{\perp} &= \sigma_1 \cos^2(\pi/2 - \theta) + \sigma_2 \sin^2(\pi/2 - \theta) \\ &= \sigma_1 \sin^2\theta + \sigma_2 \cos^2\theta \qquad \text{(iii)}\end{aligned}$$

Subtracting (iii) from (ii) and rearranging gives

$$\frac{\sigma_{\parallel} - \sigma_{\perp}}{\sigma_1 - \sigma_2} = \cos^2\theta - \sin^2\theta = 1 - 2\sin^2\theta$$

If $\sigma_1 - \sigma_2$ is small then

$$\frac{\Delta n_s}{\Delta n_o} = 1 - 2\sin^2\theta \qquad . \text{(iv)}$$

Now it is known that if fibres are spun at very slow speeds without any stretching and are allowed to contract freely in drying they are nearly isotropic [17] Fibres produced in this manner were found to approach the isotropic condition in both skin and core when examined by either the Becke or fibre refractometer methods This means that the starting condition of the fibres is one of statistical isotropy in both skin and core, *i e.*, in each case $\Delta n = 0$ If then equations (i) and (iv) are each set equal to zero it is found that for the starting condition $\phi = 54{\cdot}8°$ and $\theta = 45°$ Thus even though the fibre appears isotropic when viewed transversely the axial orientation of the skin is greater than the axial orientation of the core. The planar orientation, though isotropic transversely, will appear markedly anisotropic when viewed in the axial direction as was found by Hermans [9] Using similar considerations to those used in deriving the double refraction of the planar structure in the transverse direction, it is readily possible to derive an equation for the axial direction

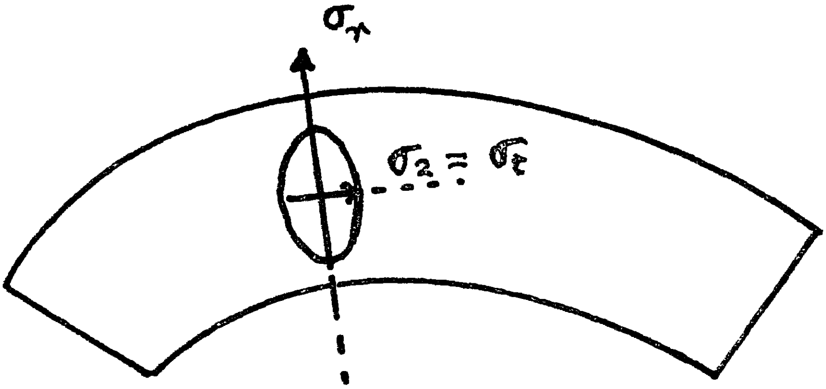

Fig 6

Let Fig 6 represent a segment of the skin of a fibre having a perfect radial planar structure Let σ_1 and σ_2 have the same significance as before and represent the polarizabilities parallel and perpendicular to the direction of the cellulose chain or chains Let σ_r and σ_t represent the polarizabilities of the skin in the transverse radial and tangential directions Then it follows that

$$\sigma_r = \sigma_1 \sin^2\theta + \sigma_2 \cos^2\theta$$

$$\sigma_t = \sigma_2$$

Hence

$$\frac{\sigma_r - \sigma_t}{\sigma_1 - \sigma_2} = \sin^2\theta$$

and with the same limitation as before

$$\frac{\Delta n_r}{\Delta n_o} = \sin^2\theta \qquad .\text{(v)}$$

where Δn_r represents the positive radial double refraction of the skin It is clear that the greater the stretch and the smaller θ becomes the smaller should be Δn_r as was observed by Hermans[9]. Hermans does not give the value for an unstretched and isotropic fibre, but it appears from the data he does give that the values calculated from equation (v) would be too high. This is because equation (v) assumes perfect planar orientation. It has already been argued that the orientation is only partially planar. The further the structure deviates from the planar one the greater will be the value of Δn_s for the skin and the less the radial double refraction Δn_r.

If the assumption is made that the skin contains a mixture of spatial and radial planar structures in the proportion of $(1-\alpha)$ and α, and if a linear mixture law is assumed then the observed value of the radial double refraction

$$\Delta n'_r = \alpha\Delta n_r + (1-\alpha)\Delta n'_c = \alpha\Delta n_r \qquad \text{(vi)}$$

since $\Delta n'_c = 0$ for light travelling along the fibre axis. In a similar way the double refraction of the skin in the usual axial-transverse directions will be less for an imperfect than for a perfect radial planar structure. Assuming the proportions of the structures as before and a simple linear mixture law the observed skin double refraction will be

$$\Delta n'_s = \alpha\Delta n_s + (1-\alpha)\Delta n_c \qquad \text{(vii)}$$

on the further assumption that the double refraction of the spatial fraction of the skin is the same as that of the core. Now from equations (iv) and (vii)

$$\Delta n'_s = \alpha\Delta n_0(1 - 2\sin^2\theta) + (1-\alpha)\Delta n_c$$

and substituting for $\sin^2\theta$ from (v) and (vi) gives

$$\Delta n'_s = \alpha\Delta n_0(1 - 2/\alpha\ \Delta n'_r/\Delta n_0) + (1-\alpha)\Delta n_c,$$

therefore

$$\alpha = \frac{\Delta n'_s + 2\Delta n'_r - \Delta n_c}{\Delta n_0 - \Delta n_c}$$

If the double refractions are expressed as the optical orientation factors $(\Delta n/\Delta n_0 = f)$ with subscripts to indicate the particular factor, α can be expressed as

$$\alpha = \frac{f_s + 2f_r - f_c}{1 - f_c} \qquad \text{(viii)}$$

To solve this equation the optical orientation factors must be known. Now Hermans has given[9] three values for Δn_r for viscose fibres stretched 10 per cent., 50 per cent. and 80 per cent., and in another publication[15] Hermans has given values of Δn_s for fibres stretched to these extents. The corresponding values of Δn_c can be derived from the data for the fibres spun into zinc sulphate given in Figs. 1 and 2. The experimental data, the derived data and the calculated values of α are set out in Table II below.

Table II

Δn_s	f_s	Δn_r	f_r	Δn_c	f_c	α
$\times 10^{-3}$		$\times 10^{-3}$		$\times 10^{-3}$		
20.5	0.436	4.7	0.10	14	0.298	0.48
29	0.616	3.6	0.07	21.5	0.458	0.55
30.5	0.65	1.7	0.036	22.5	0.48	0.46

Inevitably there is a measure of uncertainty introduced by combining data from different sources, nevertheless it is considered that the mean value of $\alpha = 0{\cdot}5$ gives the right order of magnitude to this quantity

The more oriented fibres are produced by more stretching given after the skin and core structure have been formed The spatial and the planar structures are stretched simultaneously and to the same extent The effect of the stretching on angles ϕ and θ may be expected to follow the same law whatever this is The simplest law that can be assumed is that the extension is proportional to the change of the cosine of the angle of orientation Then since both the spatial and planar structures start from the isotropic condition with $\phi = 54{\cdot}8°$ and $\theta = 45°$, after any extension

$$\cos 54{\cdot}8° - \cos\phi = \cos 45° - \cos\theta \qquad \text{(ix)}$$

With the aid of (ix) it is possible to calculate the equivalent values of ϕ and θ and with these inserted in (i), (iv) and (vii) and the value of $\alpha = 0{\cdot}5$ to calculate equivalent values of Δn_c and $\Delta n'_s$. The calculated values of θ, ϕ, $\Delta n'_s$, Δn_c and $\Delta n'_s - \Delta n_c$ are set out in Table III below.

Table III

θ	$\Delta n'_s$	ϕ	Δn_c	$\Delta n'_s\ \Delta n_c$
	$\times 10^{-3}$		$\times 10^{-3}$	$\times 10^{-3}$
45°	0	54·8°	0	0
35°	12·7	46·5°	9·4	3·3
25°	24·5	39·2°	18·9	5·6
15°	33·2	33·4°	25·7	7·5
5°	37·7	30·1°	29·3	8·4
0°	38·3	29·7°	29·6	8·7

The data of columns 2 and 4 of the table are plotted in Fig 1 as a continuous line. It will be seen from the figure that the line fits the experimental points for the fibres with marked skins Similarly a reasonable fit to the experimental points is obtained when the data of columns 2 and 5 are plotted in Fig. 2 Again the theoretical data are shown as a continuous line which agrees with the data for the fibres with marked skins

The theoretical data in Table III show that when the skin has its planar structure fully oriented, that is when $\theta = 0$, the core is still much disoriented since the corresponding value of ϕ is 29·7° This finding offers a rational explanation of why ordinary viscose fibres can be only imperfectly oriented by stretch in spinning Any stretch beyond that which completely orients the planar structure would be expected to rupture it and to produce a weak place which would cause the fibre to break in spinning The most highly stretched fibres that could be spun in the zinc sulphate containing bath nearly reached this theoretical limit as will be seen in Fig 1 None of these fibres exceeded the theoretical limit Further consideration of this line of thought suggests that the fibres spun into ammonium sulphate which have much less marked skins could have their cores more highly oriented because the cores could be stretched more before the skin planar structure began to rupture Fig 1 shows that this proved practicable since the fibres spun into ammonium sulphate could be produced with more highly oriented cores Dyeing phenomena observed with the experimental fibres described here could also be given a rational explanation on the basis of the simple structural hypothesis described here. It is hoped to discuss these phenomena in another paper.

REFERENCES

[1] Preston and Bhat *J Text Inst*, 1948, **39**, T211
[2] Freeman and Preston *Ibid*, 1943, **34**, T19
[3] Preston *Ibid*, 1947, **38**, T78
[4] Wuhrmann *Helv Chim Act*, 1945, **28**, 666
[5] Preston *J Soc Chem Ind*, 1931, **50**, T199
[6] Preston and Tsien *J Soc Dyers & Col*, 1946, **62**, 368
[7] Preston and Pal *Ibid*, 1947, **63**, 430
[8] Preston and Kapadia *Ibid*, 1947, **63**, 434
[9] Hermans XIth Internat Cong Pure & Appl Chem, 1947 Section 10 in the Press
[10] Sisson *J Phys Chem*, 1936, **40**, 343
[11] Sisson *Ibid*, 1940, **44**, 513
[12] Elod and Frohlich *vide* Schiefer and Knopf *Text Res*, 1946, **16**, 432
[13] Elod Lecture at Leeds University, May 16th, 1947
[14] Frey-Wyssling *Die Stoffausscheidung der hoheren Pflanzen*, Berlin, 1935, p 30
[15] Hermans *Contribution to the Physics of Cellulose Fibres*, Elsevier, 1946
[16] Moorhead and Sisson *Text Res*, 1945, **15**, 443
[17] Rose and Griffiths *J Text Inst*, 1948, **39**, P265
[18] Wuhrmann *Schweiz Arch ang Wiss u Tech*, 1946, Heft 1 and 2
[19] J J Hermans in ref 15, and P H Hermans and Platizek, *Koll Z*, 1939, **88**, 68

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Received 26/8/48

Letters to the Editor

[*The Institute is not responsible for the opinions of correspondents.*]

MECHANO-CHEMICAL METHODS FOR USE WITH ANIMAL FIBRES

During the conference on "Methods of Single Fibre Testing",[1] attention was drawn to the uses of mechano-chemical methods for assessing the nature and extent of the action of various reagents on animal fibres.[2] One of these methods is based on the fact that, when extension is carried out rapidly, wool fibres may be stretched 30 per cent. in water at ordinary temperatures (22·2° C.) without undergoing any significant change in elastic properties. The extent to which fibres are damaged by any treatment can, therefore, be estimated by first determining their load-extension curves up to 30 per cent. extension in water at 22·2° C. and, after subjecting them to the treatment under examination, re-determining the load-extension curves under the same conditions as before. The percentage reduction in work for 30 per cent. extension, due to the treatment, can then be calculated from the pairs of curves and affords a simple and direct measure of damage.

Although the above procedure was developed for Cotswold wool, it has since been used with other wools and human hair, in accordance with the fact that Australian Leicester wool, Australian merino wool, mohair and human hair had all been found capable of 30 per cent. extension in water without significant change in elastic properties.[3] During the course of the discussion on the above paper,[2] however, Dr. E. G. Carter suggested[4] that it might not be possible to carry out repeated 30 per cent. extensions of fibres other than Cotswold wool without a gradual reduction in the work of stretching taking place. Results obtained with a 56s New Zealand wool were quoted in support of this view, the work (in arbitrary units) for successive 30 per cent. extensions of one fibre in water being 100, 97, 82, 86, 82, 81, and 78. So great a fall in resistance to extension has never been observed in this laboratory, and as the results given by another fibre were completely different, *viz.*, 100, 99, 103, 105 and 103, it was suggested that "the conditions under which the load-extension curves were determined were unsatisfactory." Because of Dr. Carter's observations, however, it seemed desirable to confirm the results obtained in 1927 with the five kinds of fibre already mentioned, and the behaviour of Lincoln wool fibres during repeated extension in water and in 0·1N hydrochloric acid has therefore been examined.

After extraction with alcohol and ether, 5-cm. lengths were taken from the root ends of the fibres and attached to light glass hooks by means of a solution of methyl methacrylate in chloroform. The diameter of each fibre was then measured at 40-42 places along the length, before determining the load-extension curve up to 30 per cent. extension in distilled water at 22·2° C. by means of the Cambridge Fibre Extensometer. After 24 hours' rest in water, a second extension was carried out, and so on, up to eleven extensions. Although the Cambridge Fibre Extensometer does not give such precise results as the fibre balance first used in this work, it is obvious from the data of Table I that Lincoln wool fibres, like the fibres first examined, can be given several successive 30 per cent. extensions in distilled water at 22·2° C. without serious alteration in elastic properties.

Table I.

Mean diameter (μ)	Coefficient of variation in diameter (%)	Work (in arbitrary units) to stretch 30 per cent during extension number 1	2	3	4	5	6	7	8	9	10	11
33.5	5.0	100.0	102.3	101.1	101.1	100.6	101.9	100.3	98.9	98.5	100.7	97·8
41.2	6.3	100.0	100.6	98.1	98.3	97.7	99.5	97.2	96.2	95·4	97.4	94.4
50.6	5.9	100.0	101.1	99.4	98.5	97.7	98.2	96.1	95.3	94.9	96.1	93.5
33.8	6.3	100.0	102.2	100.2	99.5	100.3	101.3	98.9	97.9	98.1	99.3	96.9
37.3	5.8	100.0	101.3	100.1	100.4	100.2	99.8	97.9	97.8	98.6	99.1	96.4
40.8	8.7	100.0	101.5	100.3	99.0	98.1	100.5	97.9	96.9	95.8	98.2	95.6
39.2	6.5	100.0	101.0	100.3	98.9	98.5	99.6	98.7	96.6	97.8	98.7	97.0
37.7	7.8	100.0	102.4	100.2	100.6	99.9	100.4	98.0	98.4	97.5	99.7	95.7
40.8	6.3	100.0	100.8	99.4	98.9	96.7	98.7	96.4	95.5	95.2	96.0	94.2
57.0	7.2	100.0	100.9	99.0	97.5	97.3	97.9	96.2	95.4	95.2	95.3	94.8
32.5	16.0	100.0	98.7	94.9	92.1	93.9	92.9	91.8	—	—	—	—

Table II.

Mean diameter (μ)	Coefficient of variation in diameter (%)	Work (in arbitrary units) to stretch 30 per cent during extension number 1	2	3	4	5	6	7	8	9	10
38.5	5.3	100.0	98.8	100.4	98.3	101.4	99.2	99.3	99.6	101.7	99.6
40.4	6.1	100.0	99.7	100.2	99.1	101.3	98.8	99.4	100.5	101.4	99.7
42.5	6.8	100.0	99.9	100.0	99.4	100.5	99.4	99.9	100·3	100.6	98.7
44.7	4.8	100.0	100.3	100.4	100.6	99.8	99.2	99.4	100.1	100.8	99.7
39.0	8.2	100.0	98.8	100.1	99.0	101.3	99.4	99.8	100.3	100.6	99.7
44.2	6.6	100.0	99.9	99.3	99.9	101.4	98.6	99.2	100.1	100.4	100.0
47.8	10.7	100.0	100.5	99.8	98.8	101.3	100.0	99.2	99.8	101.3	98.5
35.9	9.7	100.0	97.9	99.5	98.7	100.9	100.0	99.4	98.1	100.2	98.2
44.2	11.2	100.0	100.0	100.9	100.3	102.3	99.6	99.8	100.3	101.3	99.8
44.5	10.5	100.0	100.0	100.2	99.8	101.6	99.1	99.5	100.0	100.9	100.6

Because each cycle of extension and contraction occupied 4 to 8 minutes, depending on the diameter of the fibre, there is a general tendency for the resistance to extension to decrease with increasing number of extensions, but even after eleven extensions the fall in resistance to extension is small except in the last case. This fibre was highly irregular in diameter, as may be seen from the value for the coefficient of variation, and the more rapid fall in resistance to extension is due to this fact, although the extension of the fibre as a whole was restricted to 30 per cent , the thinner regions must have been stretched well beyond the permissible limit, and damage is therefore excessive It has always been recognised that fibres of uniform diameter are preferable for work of this kind, but highly irregular wools may be used if the extension during calibration is reduced to ensure that no part of the fibre is seriously over-stretched.

In the second series of experiments, fibres were stretched 30 per cent several times in succession in 0 1 N hydrochloric acid at 22 2° C with, of course, a 24-hour rest between extensions. The resistance to extension was expressed as a percentage of the value obtained in the first extension in the acid solution, and the results are given in Table II.

Even after ten successive 30 per cent. extensions in acid, there is no change in the resistance of the fibres to extension. This remarkable result, which is in striking contrast with Dr Carter's, can hardly be due solely to the fact that the cycles of extension and contraction in hydrochloric acid occupied only 3 to 5 minutes It seems probable that the identity of successive load-extension curves is connected with the greater stability of disulphide cross-linkages in acid solution than in water.

Finally, in a third series of experiments, fibres were stretched 30 per cent in water, 0 1 N hydrochloric acid, and then in water again, with a 24-hour rest in the appropriate medium between extensions The results are given in Table III

Table III.

Mean diameter (μ)	Coefficient of variation in diameter (%)	Work (arbitrary units) to stretch 30 per cent during extension in —		
		Water	0 1 N HCl	Water
43 6	6 9	100 0	62 0	96 4
47 6	8 3	100 0	62 5	96 2
57 3	8 3	100·0	64 1	96 2
56 0	4 2	100 0	62 7	96 2

Using the same settings of the extensometer, other fibres were stretched twice in distilled water, and the resistance to extension on the second occasion, expressed as a percentage of that during the first, ranged from 96 4 to 99 7 for nine fibres, the average value being 97 8 It is clear, therefore, that Lincoln wool fibres can be given successive 30 per cent. extensions in water, 0 1 N hydrochloric acid and water without undergoing any serious alteration in resistance to extension

In conclusion, reference must be made to the difference between the above value of 97 8 and the corresponding data of Table I, which range from 98 7 to 102 4. The concordance within each series of results is excellent, and the difference between the two series is due to the difficulty of reproducing the original settings if the spring is removed from the extensometer between one series and the next. Under such conditions, the error in estimating the resistance to extension may be as much as ± 2·5 per cent., but if the spring is not removed, a far higher degree of accuracy is realised, as may be seen by examining the results in any vertical column of the Tables.

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Leeds University. *2nd May,* 1949.

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REFERENCES

[1] *J Text Inst*, 1947, 38, T13-T130
[2] Speakman, *ibid*, 1947, 38, T102
[3] *Idem*, *ibid*, 1927, 18, T431
[4] Carter, *ibid*, 1947, 38, T125.

To the Editor, *Journal of the Textile Institute.*

Factors Influencing the Raising of Wool Fabrics

Although there are few data on the fundamental aspects of raising wool fabrics, there are sufficient to show[1] that both the structure of the fabrics and the elastic and surface properties of the fibres are of great importance. The presence of acids and alkalies facilitates raising, as does also treatment of the fabric with chlorine, sodium bisulphite or sulphur dioxide, due, no doubt, to the effects of these reagents on the elastic properties of the fibres. Teepol—an aqueous solution of sulphated olefines—also promotes raising, although the pile produced is easily laid, and it is probable that it is the lubricating action of this reagent on the fibres which facilitates their extraction from the body of the cloth. If the presence of lubricating agents increases the susceptibility of a cloth to raising then it might be expected that anti-lubricants would reduce it, and this aspect of the theory of raising was therefore investigated as follows. Samples of cloth (2/2 twill fabric made from 64s wool) were immersed for three hours in a one per cent. solution of an anti-lubricant, Syton (a dispersion of silica) at room temperature, and then raised along with a corresponding length of untreated wool cloth on a Tomlinsons Q-Vee raising machine. One half of the treated material was processed while still wet with the Syton dispersion, but the other was dried before being raised The control sample of untreated cloth was raised dry with the treated materials, the wet and dry fabrics being separated by a considerable length of wrapper. The thickness of each raised pattern was measured under a pressure of 1 g./sq. cm. and the results, summarised in the following table, indicate clearly that the presence of anti-lubricant retards raising. Experiments carried out on cloth made from crossbred wool yielded similar results, although the differences were not quite so marked.

Fabric	Thickness of raised material (cm)
Untreated	0·44
Treated with one per cent. Syton and raised dry	0·34
Treated with one per cent. Syton and raised wet	0·39

REFERENCES

[1] Whewell, Selim and Wood, *J. Text. Inst*, 1946, 37, P198
Stevens, Whewell and Yegenaga, *J. Soc. Dyers and Col* (in the press)

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Erratum

An Enumerated Problem in Textile Design Part I By S A Shorter.

Page T197 line 12 from bottom of the page—

"For the non-sub-periodic designs, etc "

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"For the sub-periodic designs, etc."

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TRANSACTIONS

20—DESTRUCTION OF ORGANIC MATTER BY ACID ASHING, WITH PARTICULAR REFERENCE TO THE USE OF PERCHLORIC ACID IN THE OXIDATION OF TEXTILE MATERIALS

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INTRODUCTION

The separation of inorganic matter present in organic materials by the process of ashing is a long established operation, the simplicity of which overshadows a number of inherent imperfections Provision for the free access of air to the combustion leads to an equally free escape for fine particles of ash caught in random air currents, or in the reaction gases, and the employment of high temperatures causes difficulties of a chemical nature These include the reduction of certain constituents such as lead, arsenic, or antimony to a volatile condition, the occlusion of organic matter by fused salts, and the production of intractable residues as with iron, aluminium, and chromium The organic matter itself is often troublesome Suitable temperature control reduces these difficulties, but requires a muffle furnace with a reliable pyrometer attachment A defect that is particularly important when traces of metals are involved is the danger of loss by combination with the material of the crucible [4,17]

Various procedures have been proposed for the improvement of dry ashing, the best known being the addition of sulphuric acid during the process to retard reduction and volatilisation of metallic constituents The method becomes tedious if the original material is resistant to ashing, and the tendency of the acid to creep causes difficulty

The use of nitrates has been proposed to speed the oxidation of substances that are difficult to burn, and with this has been combined the use of magnesium and aluminium salts, with the dual purpose of giving bulk to the ash, and minimising the reaction of trace constituents with the crucible walls [1] In addition, the use of magnesium chloride has been suggested to prevent the formation of fusible phosphate, and the attendant inclusion of organic matter [3]

For materials containing arsenic or antimony the addition of a large excess of an alkali has been proposed,[2] but the retention of the metals has not been found satisfactory

Destruction of the organic matter by means of oxidising agents in acid media has been used successfully for some considerable time,[5] but, save when a wet process has been essential to avoid loss of volatile constituents, the dry method has generally been preferred This, presumably, has been because most acid-ashing procedures required more time and attention, and because the large volumes of reagents employed might have introduced significant amounts of impurities The high purity of modern reagents, and the availability of all-glass apparatus for their further purification when necessary have, however, largely removed the latter objection. Moreover, a satisfactory wet-ashing procedure will eliminate mechanical loss, retain volatile metals, and recover the mineral matter either in solution, or in a readily soluble form

The increasing importance of the accurate determination of traces of metals in textiles has necessitated the development of a suitable acid-ashing procedure, and in view of the favourable reports of Kahane,[10] G F. Smith,[18] and others on the merits of perchloric acid for the destruction of organic matter, the present work was undertaken to compare this method with the older procedures

Unscoured cotton yarn was used in all these comparative experiments, but an account is also given of the behaviour of cotton cloths containing various finishing agents and of other textile fibres, both natural and synthetic, when destructively oxidised with mixtures containing perchloric acid. Particular attention was directed in all experiments towards reducing to a minimum the quantities of acids employed

The fundamental requirements of an acid-ashing process are a liquid to saturate the reacting materials together with an agent capable of oxidising the organic matter completely to volatile products The agent which fulfills the former requirements is necessarily of low volatility and is usually largely unchanged by the process, though it may take some part in breaking down materials resistant to the oxidising agent The oxidising agent should be readily destroyed or eliminated, by volatilisation or other means, at the end of the process. Oxidising agents such as potassium permanganate[9] and sodium chlorate[6] leaving non-volatile residues are obviously of limited application.

In the best known procedures the conditions are met by mixtures of sulphuric acid with either nitric acid or hydrogen peroxide, but in the perchloric acid method the one reagent functions both as a high-boiling acid solvent and as an oxidising agent Perchloric acid distils at 203° C in the form of the constant-boiling mixture containing 72 per cent $HClO_4$,[11] and possesses the unique property of being an oxidising agent only when hot and concentrated [12] Under these conditions it will, for example, readily oxidise chromic ions to dichromate ions, although, when cold, even the concentrated acid will not liberate iodine from potassium iodide, the dilute acid is without oxidising action either hot or cold. It is unnecessary, therefore, to expel the excess of the acid after ashing, since its oxidising properties are lost completely when the solution is cooled or diluted for the next stage of the analysis

Perchloric acid is effective as an oxidising agent above 150° C, when decomposition occurs according to the equation $4HClO_4 \rightarrow 2H_2O + 2Cl_2 + 7O_2$ and the aqueous acid will react violently with readily oxidisable matter It is therefore necessary to effect a preliminary oxidation of the sample under milder conditions, usually by the use of another oxidant,[15] by dilution of the perchloric acid with another acid, usually sulphuric acid,[15] or by the use of a large bulk of perchloric acid [16]

When the first method is adopted, nitric acid is almost invariably used as the preliminary oxidant It boils at 121° C, and, when heated with perchloric acid, is expelled from the solution before the oxidising effect of the latter acid becomes appreciable. There appears to be no advantage, therefore, in effecting the preliminary oxidation with nitric acid in the absence of perchloric acid as advocated by some authors,[1,7,8] and in all the experiments described in this communication perchloric acid has been present throughout The use of dilute perchloric acid as the mild preliminary oxidant has been proposed[19] on the assumption that the oxidising power of the acid increases in approximate proportion to the increase in its concentration during heating. This procedure has not been tried in these laboratories, but observations made during examination of the nitric acid method suggest that the onset of rapid oxidation by perchloric acid is rather sudden, irrespective of its original concentration

Dilution of the perchloric acid with sulphuric acid has a moderating effect in the earlier stages of the oxidation. This appears to be due partly to charring of the organic matter, since perchloric acid reacts only mildly with free carbon [13,20] In the later stages, however, the dehydrating action of the acid permits of an increase in temperature above that of the constant-boiling mixture of perchloric acid, and the rate of oxidation is consequently accelerated On account of the intense charring that occurs, and the undesirably large amount of acid remaining at the end of the combustion, the method appears to have no advantage over the use of a mixture of perchloric and nitric acids In conjunction with the latter mixture, however, sulphuric acid exerts a favourable influence on the course of the oxidation, by promoting smoother boiling and by increasing the oxidising power of the solution in the later stages A mixture of the three acids has been found the most generally suitable for the destruction of materials concerned in the present work

EXPERIMENTAL

Unless otherwise stated the reagents referred to in this section are the following.—Sulphuric acid, Sp gr. 1·84 Nitric acid, Sp gr. 1 42. Perchloric acid, 60 per cent, Sp gr. 1 54 Hydrogen peroxide, 100-vol; 30 per cent, approximately

I. Oxidation of Cotton with Nitric Acid or Hydrogen Peroxide

Procedures employing either of these oxidising agents almost invariably involve the use of sulphuric acid, and, ideally, the oxidising agent is added to the hot reaction mixture at such a rate that charring by the sulphuric acid is just prevented Under these conditions the maximum useful temperature of the reaction is reached, and sulphuric acid breaks down the sample into readily oxidisable products.

The choice of a suitable reaction vessel has an important effect upon the speed and efficiency of the process. The liquid volume should be as small as possible, the loss of oxidising agent by volatilisation should be minimised by restricting the liquid surface and the recovery of particles deposited on the walls of the vessel should be facilitated by limiting the wall area to the minimum consistent with prevention of mechanical loss Boiling tubes appeared to meet these requirements most completely, and tubes 8 in × 1½ in. were used for all the experiments described in this section

The quantity of sulphuric acid required was governed by the need to saturate the sample, and to enable the amount of liquid to be kept small, compression of the cotton into pastilles[21] was essential for samples weighing more than 1 gm Concentrated acid did not wet the sample uniformly, but was rapidly absorbed in a small area, and caused intense local charring Improved performance was achieved by diluting the acid with a mixture of water and oxidising agent, the latter breaking down to some extent the absorbent structure of the cotton

Two methods of replenishing the oxidising agent during the oxidation were compared. In the first, the liquid was added directly to the hot reaction mixture from a dropping funnel, without interrupting the reaction In the second, portions of the oxidising agent were added at suitable intervals by means of a pipette, the reaction mixture being allowed to cool somewhat before each addition The former procedure required less attention, and was the more rapid for oxidation with nitric acid Dropping the acid directly into the reaction mixture proved superior to allowing it to flow down the sides of the vessel, for although the latter minimised the danger of losses through splashing, a considerable proportion of the acid was rendered ineffective by premature evaporation from the hot walls The second method was employed for oxidations with hydrogen peroxide because this reagent decomposed too rapidly when added to the boiling reaction mixture It was not necessary, however, to allow the mixture to cool to room temperature, a reasonably rapid rate of oxidation, without excessive decomposition of the reagent, being maintained by withdrawing the source of heat for about 30 seconds before each addition of the reagent, and by avoiding undue concentration of the acid

More precise details of the procedures adopted are given in the following paragraph, and data representative of a considerable number of oxidations of different weights of cotton with both reagents are recorded in Tables I and II

(i) *Oxidation with Sulphuric and Nitric Acids*

A suitable volume of the mixed acids (Table I), followed by the compressed cotton, was placed in a boiling tube (p 3) clamped vertically near its upper end, and gentle heat was applied by means of a micro-burner The contents of the tube became a pasty mass, and when this began to darken in colour heating was discontinued, and a further quantity of nitric acid was added cautiously down the sides of the tube. After the vigorous reaction had subsided heat was re-applied until the reacting mixture again began to char, when further nitric acid was added from the funnel, the addition being continued until the residual solution could be evaporated to fuming without charring Throughout the process attention was concentrated on ensuring the presence of an excess of nitric acid—evidenced by the evolution of brown fumes—to avoid conditions that might result in loss of volatile metals.[5] Particles adhering to the walls of the tube could be recovered by cautious shaking, by refluxing the residual solution, or by rinsing with small amounts of nitric acid With experience they were rarely deposited more than an inch from the bottom of the tube The residual liquid was almost invariably yellow, but the colour could be destroyed by adding about 0 1 ml of perchloric acid and boiling, it was not destroyed by hydrogen peroxide.

(ii) *Oxidation with Sulphuric Acid and Hydrogen Peroxide*

The diluted mixture (Table II) was placed in a boiling tube arranged as for the nitric acid procedure The compressed cotton was introduced, and heat applied very cautiously until slight charring occurred At this point the flame was withdrawn, and the contents of the tube were allowed to cool somewhat before adding a further quantity of hydrogen peroxide Heating was then resumed, and continued until charring again began to occur, the sequence of operations being repeated until the solution could be evaporated to fuming without appreciable darkening To ensure the presence of an excess of the oxidising agent throughout the process, fresh additions were always made before the reaction mixture had darkened beyond a chocolate brown colour. The final solutions were always colourless, but frequently contained residues of waxy material, presumably cotton wax, which proved very resistant to attack by this method.

Table I
Wet Oxidation of Cotton Yarn by Sulphuric and Nitric Acids

Weight of sample (gm.)	Composition of initial mixture			Volume of nitric acid added subsequently			Time for complete destruction (min.)
	Sulphuric acid (ml.)	Nitric acid (ml.)	Water (ml.)	After first charring (ml.)	Later addition (ml.)	Total (ml.)	
0·5	1	1	2	1	1	3	30
1·0	2	1	4	4	1	6	35
2·0	2·5	1	4	4	2	7	40
3·0	3	1	5	5	4	10	45
4·0	4	3	5	8	8	19	55
5·0	5	3	7	15	8	26	80

Table II
Wet Oxidation of Cotton Yarn by Sulphuric Acid and Hydrogen Peroxide

Weight of sample (gm.)	Composition of initial mixture			Volume of hydrogen peroxide added subsequently			Time for complete destruction (min.)
	Sulphuric acid (ml.)	Hydrogen peroxide (ml.)	Water (ml.)	After first charring (ml.)	Later addition (ml.)	Total (ml.)	
0·5	1	1	2	1	1·5	3·5	30
1·0	2	2	3	2	2	6	40
2·0	2	2	3	3	7	12	40
3·0	3	3	3	5	11	19	45
4·0	4	4	4	10	12	26	55
5·0	5	5	5	10	12	27	60

II. Oxidation of Cotton with Mixtures containing Perchloric Acid

Some difficulty was experienced in the selection of a vessel that would permit rapid evaporation of excess nitric acid and water after the preliminary oxidation, and avoid loss of material during the rapid and copious evolution of gases occurring during reaction with the perchloric acid. Initially, when the safety of the reaction was in doubt, a tall 600 ml. beaker covered with a clock glass raised on glass hooks was used. With a vessel of this type, however, considerable losses occurred, presumably as a result of spirting, and the large wall area rendered the complete destruction of deposited organic matter somewhat difficult. The large liquid surface essential for rapid evaporation was maintained, and the wall area effectively reduced by the use of conical flasks fitted with removable necks (Fig. 1) to prevent mechanical loss. These necks were easily constructed by drawing out the end of suitable boiling tubes or test tubes, the approximate lengths for flasks of different sizes being 500 or 250 ml.—7 in., 100 or 50 ml.—5½ in. For very small amounts of material special 10 ml. conical flasks with necks 3 inches long were constructed. Analyses conducted with the aid of these vessels showed that mineral constituents were quantitatively retained. Compression of the cotton was found to be unnecessary, and quantities up

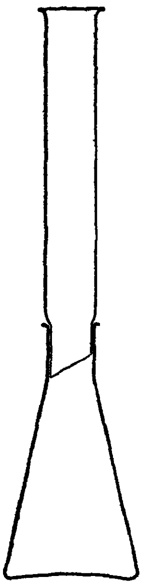

Fig. 1

to 5 grams of loose yarn were destroyed without difficulty. Since all the reactants were present from the start, the rate of heating was the sole controlling factor of the reaction. The effect of this is shown in Table III. When the flasks were heated on a wire gauze over a Bunsen flame, the reaction was difficult to control, and its course in nominally identical oxidations varied widely. The most satisfactory results were obtained by the use of a graded hot plate, 11 in × 9 in. × ⅜ in., heated by a rack of five micro-burners placed parallel to, and about 2 inches from, one of the longer edges. Holes were drilled in the middle of each of the longer edges, and thermometers inserted in these holes to a depth corresponding roughly with the centres of 250 ml. flasks standing at the edges of the plate, indicated reasonably constant temperatures. Temperatures of 200° and 325° C. respectively gave satisfactory results. The flasks were placed on the cooler side of the plate, and moved towards the hotter side as the reaction proceeded, fresh flasks being added as space became available. A considerable number of oxidations could thus be conducted concurrently.

Table III

Destruction of 4 gm. of Cotton Yarn with mixed Perchloric and Nitric Acids

Temperature of plate under vessel (°C) .	290	250	225	200
Time for destruction (mins.) . .	10	15	30	50

(i) *Oxidation with Mixtures of Perchloric and Nitric Acids*

The sample was introduced into a conical flask containing suitable quantities of the two acids (Table IV), an extension tube was fitted, and the flask placed on the cooler side of the hot plate. After a short time, the sample commenced to react with the nitric acid, forming a pasty mass, which was slowly converted to a clear, slightly green solution. At this stage the flask had been moved far enough towards the hotter side of the plate to cause the contents to boil fairly rapidly. When excess nitric acid and water had been expelled, the rapidly increased rate of ebullition, with production of dense white fumes, showed that the perchloric acid reaction had commenced. The intensity of the reaction was moderated, when necessary, by moving the flask back towards the cooler side of the plate. When the vigorous reaction had subsided the flask was moved to the hottest part of the plate, and the residual acid was boiled until the level of condensation had reached well into the extension tube, which was raised two or three times at this stage to release the liquid held by surface tension between the tube and the neck of the flask. The flask was then allowed to cool somewhat, and the contents were diluted with water (50-100 ml.), the extension tube being rinsed and removed. The solution was boiled for two minutes to expel the chlorine liberated in the reaction, a boiling rod being used to prevent "bumping". Typical data for a number of oxidations are given in Table IV.

Table IV

Oxidation of Cotton Yarn by Perchloric and Nitric Acids

Weight of sample (gm.)	Perchloric acid (ml.)	Nitric acid (ml.)	Residual perchloric acid (ml.)	Time for complete destruction (min.)	
1	5	4	2.5	8	250 ml. flasks
2	7	7	3	10	
3	9	10	3	10	
4	12	15	5	14	500 ml. flasks
5	15	18	4.5	16	

A blackening of the solution, due to charring of the dissolved organic matter, was occasionally encountered during this process, presumably when the excess nitric acid had been removed completely and before the perchloric acid was sufficiently concentrated to act as an effective oxidising agent. The darkening invariably started at the hottest side of the flask, and was frequently observed to radiate from a single point Swirling of the contents of the flask or addition of a small amount (0·1 ml.) of concentrated nitric acid sufficed to overcome the trouble in its early stages and avoided development of reducing conditions that might have resulted in loss of any volatile metals present.[14] The tendency to char was diminished by prolonging the preliminary oxidation with nitric acid and as charring always tended to retard the reaction and to give a solution difficult to decolourise, nothing was gained by attempting to accelerate the first stage of the operation unduly. The darkening of hot concentrated perchloric acid in the presence of organic matter is frequently stated to indicate impending explosion,[21] but when using a preliminary oxidation as described the only effect of charring has been to make the reaction inconveniently slow. The normal speed has been restored immediately on dispersing the char with nitric acid.

(ii) *Oxidation with Mixtures of Perchloric, Nitric and Sulphuric Acids.*

The procedure was similar to that described above When operating in the absence of sulphuric acid it was found that, after the perchloric acid reaction had abated, the high surface tension of the residual acid caused it to be drawn away completely from some parts of the bottom of the flask unless a considerable volume remained. This resulted in a sharp rise in the temperature of the bare patches with attendant risks of cracking the flask, and of possible volatilisation of mineral constituents from spray falling on these parts; moreover, the marked tendency of the acid to become superheated resulted in excessive bumping Addition of as little as 1 per cent. of sulphuric acid on the volume of perchloric acid effected a marked improvement and in practice it was found possible to replace by sulphuric acid a substantial part of the perchloric acid not consumed in the reaction, and to save 10-20 per cent. of the more costly acid. This substitution, however, resulted in increased incidence of charring, which could be overcome to some extent, with the larger samples, by increasing the proportion of nitric acid in the reaction mixture Charring developing during the reaction was dispersed by the methods previously given.

Typical data are given in Table V

Table V

Oxidation of Cotton Yarn by Perchloric, Nitric and Sulphuric Acids

Weight of sample (gm.)	Perchloric acid (ml.)	Nitric acid (ml.)	Sulphuric acid (ml.)	Residual acid (ml.)	Time for destruction (mins.)	
1	3·5	3·5	1	3	10	250 ml flasks
2	6·5	6·5	1	4	13	
3	8	11	1	3·5	16	
4	11	16	1	4·5	10	500 ml. flasks
5	14	20	1	6	17	

III. The Destruction of Textile Fibres other than Cotton and of some Typical Finished Cotton Cloths with Perchloric, Nitric and Sulphuric Acids

In the experiments described in this section the weight of material used varied between 1 and 3 grams and, except where otherwise stated, the oxidations were performed in 250-ml conical flasks fitted with removable extensions as described in the preceding section. Rayon, nylon, silk, and wool were used in the form of yarn or fibre without compression. The finished materials included cotton cloths coated with drying oil, rubber, polyvinyl chloride, and paraffin wax. The compositions of the acid mixtures most generally satisfactory for each material are summarised in Table VI, which includes the approximate times taken for complete destruction of the organic matter and the corresponding times for the normal dry ashing process.

Table VI

Destruction of Textile Fibres other than Cotton and of some typical Finished Cotton Materials

Material	Weight (gm)	Composition of oxidising mixture			Time for complete destruction (min)	Time for comparable dry-ashing (hours)	Remarks
		Perchloric acid (ml)	Nitric acid (ml)	Sulphuric acid (ml)			
(1) Viscose or cuprammonium rayon	1	3	4	1	10	1–2*	H_2SO_4 completely replaceable by $HClO_4$†
	2	4	10	1	15		
	3	6	15	1	18		
(2) Acetate rayon	1	3	2	1	10	2*	As above†
	2	6	4	1–2	12		
	3	9	6	1–3	15		
(3) Nylon	1	4	4	1	12	1·5*	As above†
	2	8	8	1–2	15		
	3	12	12	2–3	20		
(4) Silk (raw or degummed)	1	4	3	1	8	2–3*	Destruction less satisfactory without H_2SO_4
	2	8	6	2	15		
	3	10	8	3	20		
(5) Wool	1	4 5	2 5	1	10	3*	H_2SO_4 completely replaceable by $HClO_4$
	2	6	6	2	15		
	3	7 5	10	2	20		
(6) Oil-proofed cotton cloth	1	4	4	1	20	0 5	As (5)
	2	6	6	2	25		
	3	9	9	2	30		
(7) Cotton cloth proofed with polyvinyl chloride	1	4	2	1	15	1	H_2SO_4 must be present at least in the amounts indicated
	2	8	4	2	20		
	3	12	6	3	25		
(8) Cotton cloth proofed with rubber	1	3 5	2 5	1	12	0 5	As (5)
	2	6 5	5 5	1	17		
	3	9	10	1	23		
(9) Cotton cloth proofed with paraffin wax	1	4	4	1	10	0 5	As (5)
	2	7	8	1	14		
	3	9	12	1	16		

* Including time occupied in preparation of pastilles.

† Titanium dioxide may be present as a delustrant, and will dissolve fully only in the presence of sulphuric acid

In the study of these reactions an attempt was made to find a mixture of acids which would give speed without undue vigour, and repress charring as far as possible. The volume employed was to be kept at a minimum An initial test was made with an excess of a mixture of nitric, perchloric and sulphuric acids, and the general course of the reaction was noted. The residual acid was measured and the volumes of the non-volatile acids were reduced to give a residue of from 2 to 4 ml when using a 250-ml. flask, which was increased up to 6 ml. when dealing with material substantially unattacked until the perchloric acid stage of the reaction.

A series of tests were next performed to determine the minimum quantity of nitric acid required A deficiency was indicated by increase in the tendency to char during the evaporation immediately preceding the perchloric acid reaction, and by an appreciable decrease in the volume of the residual acids Finally, the effect of varying the proportions of the non-volatile acids was investigated, with particular reference to the behaviour of the ash in the absence of sulphuric acid The optimum conditions of heating were determined by experience as familiarity with the reaction increased

Some compromise short of an ideal reaction was usually necessary as is indicated in the descriptions, and the figures quoted are those found to give the most satisfactory results under the conditions used

(i) *Viscose and Cuprammonium Rayons.*

These behaved identically, but differed from cotton in forming no pasty mass at the start of the reaction They passed readily to a clear yellow solution. The reaction with nitric acid was more protracted, and the subsequent reaction with perchloric acid, therefore, considerably milder than with cotton A marked tendency to char at the start of the second stage was reduced by decreasing the proportion of sulphuric acid, and by heating more slowly

(ii) *Cellulose Acetate Rayon.*

This material gelatinised in the cold acids, but dispersed on heating to give a clear yellow solution. There was a tendency, however, for a thin film of molten material to float upon the surface of the mixed acids, and thus to escape the full preliminary oxidation This charred later, giving aggregates that were difficult to disperse, but there was no indication of hazard (*cf.* polyvinyl chloride, p 10) The trouble was minimised by moderating the heating, particularly during the early stages of the oxidation with nitric acid. The acetylation of the cellulose appeared to moderate the whole reaction.

(iii) *Nylon.*

The fibre gelatinised, and dissolved in the cold acids. The nitric acid reaction was brisk, but the perchloric acid reaction developed slowly, and was usually accompanied towards its end by charring, and by sufficient foaming to necessitate the use of 500-ml flasks for samples weighing more than two grams * The considerable charring was not readily dispersed by addition of nitric acid, and the full heat of the plate was required to clear the solution This became colourless, but owing to the presence of titanium dioxide, a delustrant in the original material, it remained turbid throughout the reaction and cleared during the final refluxing only when sulphuric acid was present. Acetic acid vapour was evolved during the oxidation, and a heavy deposit of ammonium perchlorate remained in the flask

(iv) *Silk*

The sample reacted immediately with the cold acids to form a rigid, structureless, yellow jelly, which broke down slowly on standing and rapidly when the flask was heated The reaction with nitric acid was unusually mild and liberation of brown fumes from the yellow solution at the start of the perchloric acid reaction suggested than an appreciable amount of compound formation had occurred. Although vigorous, the perchloric acid reaction was less rapid than with cellulose, and tended to produce charring which was reduced by prolonging the preliminary oxidation at a relatively low temperature. Once formed, the charred material was not easily dispersed by nitric acid, and left a yellow solution which, however, cleared fairly rapidly on boiling. Some product of the reaction appeared to be resistant to perchloric acid and the presence of sulphuric acid was found to be essential to obtain rapidly a clear, colourless residue Raw and degummed silk exhibited no significant differences.

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*Addition of trichloroacetic acid, as suggested by Smith and Deem[20] did not reduce frothing.

(v) *Wool*

The wool rapidly absorbed the cold acids, with some disintegration of the fibre to form a yellow, somewhat gelatinous mass The material was heated in this condition, and after slight intumescence passed rapidly to a clear yellow solution which passed smoothly through the remaining stages The reaction with perchloric acid was somewhat brisk In the earlier experiments it was noticed that on the collapse of the initial intumescence the material tended to catch fire This was traced to the presence of wool that had escaped wetting by the acids, and further trouble was avoided by shaking the sample with the cold acids until it was thoroughly wetted Charring tended to occur with increasing sample weight, but was readily dispersed by adding nitric acid. It could be eliminated by prolonging the preliminary digestion at a relatively low temperature

(vi) *Oil-proofed Cotton Cloth*

Rapid reaction commenced on heating accompanied by considerable intumescence, which collapsed abruptly to give a dark yellow solution overlaid by oily matter. Boiling, with some frothing, continued with gradually increasing speed until the start of the perchloric acid reaction was quietened by a sudden charring Frothing then commenced to build up again, and the solution cleared slowly The charring could be dispersed readily by the addition of nitric acid, or prevented by prolonging the preliminary digestion and increasing the amount of sulphuric or perchloric acid. A tendency for particles of the material to ignite immediately after the collapse of the first intumescence was traced, as with wool, to imperfect wetting by the acids. It was avoided by cutting the sample into fragments not exceeding ¼ inch square, diluting the acids with water equal to half the volume of the nitric acid used, and shaking the material thoroughly with the mixture before heating. Dilution with water was particularly desirable in the case of mixtures that did not contain sulphuric acid

(vii) *Cotton Cloth coated with Polyvinyl Chloride.*

The nitric acid rapidly stripped the plastic from the cloth, the former floating with little apparent change until the rise of temperature following elimination of the nitric acid caused it to char. The floating charred aggregates were slowly destroyed by continued gentle heating and the full heat of the plate was applied only when the aggregates appeared to be carbonised completely, premature heating on the hottest part of the plate resulted in general charring throughout the liquid and necessitated further additions of nitric acid

The floating plastic was found to be a source of danger. On one occasion, when working in the absence of sulphuric acid, a violent explosion occurred at the perchloric acid stage, while a similar attempt with a mixture containing only a small proportion of sulphuric acid resulted in a mild explosion. Fires were encountered in other experiments in which slightly more sulphuric acid was used When, however, the volume of sulphuric acid was at least one quarter of that of the perchloric acid no trouble was experienced in a total of thirty experiments. As additional precautions, a relatively large volume of mixed acids was used and the preliminary digestion in the presence of nitric acid was prolonged The trouble was ascribed to the sudden release in the later reaction, possibly by melting, of readily oxidised constituents of the plastic mix previously protected from the nitric acid

(viii) *Cotton Cloths proofed with Rubber.*

Cloths containing up to 40 per cent of proofing were used, but the amount of rubber was insufficient greatly to affect the course of oxidation.

The nitric acid reaction followed a normal course, but the rubber appeared to be largely unaffected, and remained as a scum on the surface. The onset of the perchloric acid stage was accompanied by considerable frothing and some charring The latter was not readily dispersed by additions of nitric acid, but colourless solutions were obtained without difficulty. Heavy white precipitates due to inorganic fillers were present throughout, but these did not appear to affect the course of the oxidation or cause serious "bumping"

(ix) *Cotton Cloths proofed with Paraffin Wax.*

The wax was largely removed from the fabric at an early stage and formed a film on the surface of the liquid This retarded evaporation of the acids which therefore required to be heated rather strongly to maintain a reasonably rapid rate of destruction Soon after the start of the perchloric acid reaction the wax became charred with the formation of discrete particles. These were readily destroyed by the boiling acid, or even more readily by the addition of a few drops of nitric acid, but it appeared to be impossible to prevent charring without prolonging the reaction unduly.

DISCUSSION

When the time occupied in dissolving a dry ash is considered, the wet-ashing procedures using sulphuric acid and either nitric acid or hydrogen peroxide are comparable in speed with normal dry methods Considerable attention is required, however, when using nitric acid, and almost continuous attention with hydrogen peroxide. Moreover, both methods, and particularly the latter, tend to leave residues of any fat and wax that may be present in the original materials

Time is important in analytical work, and an outstanding feature of the perchloric acid procedures is their speed which is maintained even with materials such as silk, wool, and acetate rayon, where dry ashing is troublesome This, together with the wide applicability of the process, the small amount of attention required, and its suitability for routine work renders it much superior to the other wet procedures described, and makes it a serious rival to dry ashing. Despite numerous instances of its safe application,[11,19] perchloric acid is still generally regarded as a hazardous reagent, and some consideration of its properties and the simple precautions necessary for its use as an oxidant appears to be desirable

The concentrated perchloric acid available commercially, namely, 60 per cent. or 70 per cent., is stable indefinitely, either alone, or when mixed with nitric or sulphuric acids. The only potentially dangerous form is the hot, concentrated acid, and although the exact limits of temperature and concentration at which this becomes dangerous vary according to circumstances, all concentrations may be considered to be inert at room temperatures The hot, concentrated acid reacts violently with readily oxidisable material, either organic or inorganic, and when employed as an oxidant a preliminary partial oxidation with a milder oxidising agent, nitric acid, is necessary to avoid the risk of serious accidents As a safeguard against inadvertent omission of nitric acid, it is desirable when preparing the oxidising mixture, to measure the nitric acid first. Accidental omission of the nitric acid from a reaction mixture is evidenced by immediate charring on heating, and should be dealt with by removing the flask from the hot-plate, or by diluting its contents with water

Condensation of the vapour of perchloric acid on wooden laboratory structures, particularly fume cupboards, has been suggested as a potential source of danger arising from the evaporation of residues of the acid at the end of the ashing process.[21] Although the acid distils under atmospheric pressure as the constant-boiling mixture containing 72 per cent of $HClO_4$, the chance of the condensate *in situ* reaching a temperature at which its oxidising power is appreciable seems very remote. Likewise, the elaborate storage precautions frequently suggested for the aqueous acid are unnecessary.

Safety precautions must always be taken when dealing with previously untried materials A screen of reinforced glass was used throughout the present work for each substance under investigation until the safety of the reaction had been established, but in upwards of a thousand ashings of the various materials used, only one seriously violent reaction was encountered (see p. 10) It cannot be too strongly emphasised, however, that perchloric acid can, and will, react violently under certain conditions, and no attempt should be made to use it on untried materials without a thorough understanding of its properties. Once a given reaction has been carefully studied and reduced to a routine procedure demonstrably free from hazard, it may be confidently left to semi-skilled workers who must, however, be warned of the dangers of departing from the prescribed conditions

The occurrence of reducing conditions at certain stages of the reaction, which may lead to loss of certain mineral constituents should be remembered when applying the procedure. The critical period lies between the expulsion of the nitric acid and the commencement of the perchloric acid reaction, and its development is associated with the appearance of charring at this stage Kahane[14] has observed loss of arsenic in this manner and the author, loss of antimony (unpublished work). Methods of overcoming the reducing conditions have been considered in the experimental section

SUMMARY

The use of perchloric acid in the wet oxidation of textile material has been shown to be superior to the use of the more classical reagents in speed and convenience In many cases the procedure is superior to the dry methods normally employed.

Simple and safe procedures have been evolved for the wet destruction of a number of diverse textile materials, and the principles governing the employment of perchloric acid have been discussed.

BIBLIOGRAPHY

1 American Society for Testing Materials Standard D377-47.

2 Bamford *Analyst*, 1934, **59**, 101

3 Bandemer and Schaible *Ind Eng Chem* (*Anal Ed.*), 1944, **16**, 417

4 Comrie *Analyst*, 1935, **60**, 532

5 Cox *Analyst*, 1925, **50**, 3

6 Erdos and Groàk *Magyar gyógyszerésztud Társaság Ertesitoje*, 1933, **9**, 397-399; through *Chem Zentr*, 1933, ii, 3166

7 Gerritz *Ind Eng Chem*, (*Anal Ed*), 1935, **7**, 167

8 Gieseking, Schneider and Getz *Ibid* p 185

9 Jacobs "Analytical Chemistry of Industrial Poisons, Hazards and Solvents", Interscience Publishers, N Y, 1944, p 189

10 Kahane "L'Action de L'Acide Perchlorique sur les Matières Organiques", Herman et Cie, Paris, (*Actualités Scientifiques et Industrielles*, Nos 167, 168)

11 *Ibid*, p 12

12 *Ibid*, p 17

13 *Ibid*, p 25

14 *Ibid*, p 27 and p 66

15 *Ibid*, p 33.

16 *Ibid*, p 45

17 Ridge, Corner and Cliff *Shirley Inst Mem*, 1933, **12**, 23 and *J Text Inst*, 1933, **24**, T293

18 Smith, "Perchloric Acid," and "Mixed Perchloric, Sulphuric and Phosphoric Acids and their Applications in Analysis", The G Frederick Smith Chemical Co, Columbus, Ohio

19 Smith, "Mixed Perchloric, Sulphuric and Phosphoric Acids etc," p 11

20 Smith and Deem *Ind Eng Chem*, (*Anal Ed*), 1932, **4**, 227

21 Willard and Diehl "Advanced Quantitative Analysis", Van Nostrand, 1943, p 8-9

22 Williams *Shirley Inst Mem*, 1923, **2**, 225-226 and *J Text Inst.*, 1923, **14**, T295

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21—THE ESTIMATION OF FATTY MATTERS IN WOOL

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An account of an investigation into the natures and methods of estimation of the fatty matters normally present on wool during its processing, the errors and sources of interference therein, and the conclusions reached in the light of the results.

Introduction

The importance of the amounts of the different fatty matters which may be present on wool, whether as natural fats or artificial additions, can hardly be over-emphasized They play a critical part during almost every stage of processing as is well known, confirmation being afforded by the volume of literature published on the subject

Portions of this literature, however, tend to be contradictory in nature, and indeed, the methods practised over the whole field of analysis of fatty residues on wool seem to lack uniformity For instance, whilst the Commercial Scour Test is still the standard recognised by the industry for the estimation of total fatty matter, the solvent extraction method is probably more widely employed The latter method itself suffers from the disadvantage that there is no standard solvent, or even procedure, in general use

The present work, therefore, was undertaken with a view to investigating the different methods which can be employed, and elucidating the natures of the various fatty matters which have to be dealt with, in order to find the methods of estimation which are most suitable for general use.

In the first place, the fats normally encountered can be broadly classified into three groups —

(1) Residual fats derived from wool grease
(2) Added lubricating oils
(3) Soapy residues.

The effects of residual wool fat and added oil on the processing and general attributes of wool need no discussion here The soap residues, however, which are actually the alcohol-soluble matters which remain on wool after initially removing true fats by another solvent such as diethyl ether, must also have comparable effects by virtue of their own unctuous and sticky nature It may therefore be thought somewhat strange that their estimation is not generally requested to anything like the same extent as that of the true fatty matters. This may be because the proportion of them is not subject to the same degree of control as are the proportions of added oil and residual wool fat, but it is later shown that the soap residues are intimately bound up with the estimation of the other fats, and their importance is thereby considerably enhanced

A survey of some of the literature published to date follows

Woodmansey[1] first extracts fatty matter from wool by means of petroleum ether. This process is followed by short immersion of the wool in boiling 1 per cent hydrochloric acid solution, squeezing and air-drying The liberated fatty acids present on the dried wool are then extracted with ether, and their equivalent as soap calculated If any oxidised fatty acids are likely to be present, Woodmansey recommends methylated ether in place of petroleum ether for the initial extraction of fat

Hummel[2] and Maercker and Schulz[3] extract raw wool with ether and remove what they term soluble oleates by shaking the ether with water They repeatedly extract the fat-free wool with cold distilled water, adding the extracts to the washings separated from the ether Thirdly, the wool is extracted with alcohol, and the "oleates" thus dissolved are added to the aqueous solution. The total amount of oleates in these bulked extracts is determined, after which the wool is treated with dilute hydrochloric acid to split up earthly oleates not previously removed The acidified wool is washed, dried and then extracted in succession with ether and alcohol From these solvents, on evaporation, oleic acid is obtained corresponding to the original earthly oleates.

King[1] says the petroleum ether used in Hummel's method extracts notable quantities of soap, which he suggests is composed of acid soap His own procedure is to perform an initial extraction of a wool sample with petroleum ether for the purpose of removing oil, this extract being examined for soap by boiling with distilled water and titrating with N/10 hydrochloric acid The sample is then extracted for 5 to 6 hours with hot alcohol to remove soaps, the solution being filtered and evaporated The soap content is estimated from the amount of N/10 sulphuric acid needed to acidify (against methyl orange) the alcoholic extract dissolved in water. Following this, the acidified solution is shaken with ether to remove all fatty matter, and the latter recovered by evaporation of the ether In this recovered fatty matter the total fatty acids are estimated by titration of their solution in alcohol with N/10 caustic potash or soda King estimates calcium (as oxalate) in the aqueous solution which results from the soap estimation

The method of Trotman[5] is to extract fat by petroleum ether Extraction for three hours with absolute alcohol follows, which is said to extract sodium and potassium soaps. From this alcoholic extract fatty acids are obtained by acidification and extraction with ether. The acid used in acidification is measured and the soap content calculated therefrom. After this treatment calcium and magnesium soaps are supposed to remain on the wool, and are estimated (as fatty acids) by soaking the sample in dilute hydrochloric acid for one hour and extracting with ether in Soxhlet apparatus

Gilmore[6] recommends benzene or carbon tetrachloride as a solvent for oleate soaps and a mixture of benzene/alcohol (9/1) for stearate soaps He finds, as did Woodmansey,[2] that in extracts of soap an excess of fatty acids over alkali prevails, and attributes this to partial hydrolysis of the soap residues during extraction He also finds, in agreement with Trotman, that even after extraction of wool with alcohol small amounts of soap still remain absorbed, but suggests that these are not calcium and magnesium soaps and owe their non-extraction to the nature of their fatty acid components, which (he says) are possibly of the oxidised type

Successive ether and alcohol extractions are also employed by Von Bergen,[7] who finds that oxidation reduces the amount of ether-solubles, but gives simultaneous increases in the alcohol-soluble matter

Ryberg[8] extracts fat by a two-hour treatment with ethyl ether, and soaps by a subsequent six-hour extraction with 95 per cent alcohol Residual calcium and magnesium soaps are estimated by a third extraction with formic acid-acidified ethyl ether An overlapping effect between ether and alcohol is suggested, ether removing unoxidised and oxidised oils, together with some hydrolised fatty acids, alcohol removing oxidised oils, soap, higher alcohols and free and esterified sterols In addition he gives an analysis of some soap residues extracted by alcohol.

The foregoing will, no doubt, give some idea of the complexity of the problems which have to be faced in this work, at least from the point of view of the solvent-extraction method The Commercial Scour Test is discussed separately, later in the paper

It is apparent that the estimation of all fatty or fat-containing substances on wool is essentially a three stage process. In the first place true fats such as residual wool fat and added oils are determined, this process being followed by removal of the alcohol-soluble soap residues and, finally, the estimation of any alcohol-insoluble soap residues still remaining on the wool.

These three stages are now discussed in turn

Estimation of Total Fatty Matter

The term "Total Fatty Matter," when used with reference to wool, is normally understood to represent the true fats, such as wool fat and added oil, as opposed to soaps.

The general procedure for estimation of the Total Fatty Matter by solvent-extraction is to employ a Soxhlet apparatus, about 10 gms. of wool being extracted for the period considered suitable (usually 2 to 3 hours) with a solvent, usually diethyl ether. Some workers make use of a Soxhlet thimble, while others dispense with this and instead filter the ethereal solution before evaporation and weighing of the dry residue of fats. In addition to this non-uniformity, diethyl ether, as has been previously mentioned, is not a general standard for the solvent. Since the solvent to be used must be the first consideration, five of the most likely ones have been extensively compared

The Effect of Varying the Solvent

Four samples drawn from the same wool top were submitted to extraction with different solvents, the weight of each sample being 10 to 12 gm and 120 ml. of solvent being used in each case The rates of extraction were adjusted so as to be as nearly equal as possible, with an average period of syphoning of about 2 minutes.

No Soxhlet thimbles were used, the solutions being filtered before evaporating and finally drying the residues, first for ten minutes in an air oven at 105-110° C., and finally in a desiccator

The top was an Australian 64s quality, combed in B.M (Blended Mineral) Oil.

Table I

	Dichloro-ethylene	Chloroform	Diethyl ether	Petroleum ether (40-60°C)
Fat extracted after 3 hours	4 034%	3 970%	3 721%	3·627%
Free fatty acids (as oleic) in extract	8 83%	9 35%	7 75%	5 77%

In order to ascertain whether the type of combing oil had any effect, the experiment was repeated on a wool top, combed in Class "A" Control Oil, but otherwise of a similar type Also, acetone was substituted for dichloro-ethylene in order to extend the range of solvents.

Table II

	Acetone	Chloroform	Diethyl ether	Petroleum ether
Fat extracted after 3 hours	3·798%	3·788%	3·516%	3·363%
Free fatty acids (as oleic) in extract	6·34%	6·40%	4·27%	2·05%

From the two sets of results, the type of combing oil appears to have no significant effect. According to which solvent is used, however, a markedly different result is obtained.

The petroleum ether extract is, in each case, the least in amount. This may be largely explained by the insolubility in petroleum ether of certain of the wool grease fatty acids, since up to 39 per cent of these can be present in the oxidised state.[9] In addition, oxidised acids are likely to be present in the added oil where the combing is not of a very recent date, and such oxidised fatty acids are known to be insoluble in petroleum ether. The relatively low percentages of free fatty acids in the petroleum ether-extracts are in agreement with this theory, and although they alone do not prove it, more evidence is forthcoming later.

In view of this incomplete extraction when petroleum ether is used, it is rather surprising that some workers still prefer it. Actually, in the two cases quoted above, the difference between the petroleum ether and diethyl ether extracts is of the order 0·1 to 0·15 per cent. only, but in general much larger differences have been encountered, of the order 0·2 to 0·3 per cent.

An exceptional case, an Australian Merino wool in the scoured state gave the following results:—

Table III

Fatty matter (extracted by petroleum ether)	0·53%
Fatty matter (subsequently extracted by diethyl ether)	0·49%

Here, in order to avoid error due to uneven distribution of fat on the wool, the same sample was used in each extraction, the diethyl ether treatment being subsequent to that of petroleum ether.

In the case of raw or greasy wools, there is usually an even larger percentage of fat which can be extracted by diethyl ether following an initial petroleum ether-extraction.

The wool used for the tests in Table III, when examined in the greasy state, gave the following results:—

Table IV

Fatty matter (extracted by petroleum ether)	14·54%
Fatty matter (subsequently extracted by diethyl ether)	0·90%

The three solvents, acetone, dichloroethylene and chloroform, are each seen to give more extract than either of the other two, and, moreover, the extracts are higher in free fatty acids. This fact might, of course, be merely due to certain constituents of the fats being less soluble in either ether than the other three solvents, but this does not seem a very likely explanation, since diethyl ether especially is a very good solvent for fats in general.

A suggested explanation of this phenomenon is given later under the next heading.

Influence of the Time of Extraction

Since the time for which a sample is extracted is plainly important, a trial was carried out using the same four solvents and general procedure as before. In this case, however, the respective fatty matter extracted by each solvent was estimated after regular intervals in an attempt to determine when the extractions were completed. The wool was a 64s blend combed in B.M. (Blended Mineral) Oil, the following results being obtained.—

Table V

Solvent used	Percentage of extract during					
	1st Period (1½ hrs.)	2nd Period (1 hr.)	3rd Period (1 hr.)	4th Period (1 hr.)	5th Period (1½ hrs.)	Total Extract (6 hrs.)
Diethyl ether	3·720	0·090	0·015	0·025	0·030	3·880%
Petroleum ether	3·609	0·013	0·007	0·005	0·006	3·640%
Chloroform	3·801	0·130	0·060	0·015	0·046	4·052%
Dichloroethylene	3·756	0·078	0·034	0·030	0·030	3·928%

These figures show that the extractions were virtually complete after about 3 hours. Over the total period tested, however, none of the extractions reached absolute completion, with the possible exception of the case of petroleum ether. A more or less constant small amount was extracted by each solvent during the last three periods.

This might have been due merely to constituents of the fat being only slightly soluble in the solvents, but an explanation considered to be much more likely was that hydrolysis of the soap residues still on the wool was taking place. This was in agreement with Ryberg's findings, but further confirmation was desired.

From the same wool as was used in Table V experiments, four more samples were taken, as large as could possibly be accommodated in the Soxhlet extractors.

Each was extracted for 2½ hours with one of the four solvents, and the percentages of extract determined. The same samples were then extracted with their respective solvents for a further period of five hours, and the secondary extracts determined.

Table VI

	Dichloro-ethylene	Chloroform	Diethyl ether	Petroleum ether
Initial extract	3·825%	3·865%	3·657%	3·543%
Free fatty acids (as oleic) in extract	6·12%	8·66%	5·06%	3·11%
Secondary extract	0·141%	0·163%	0·109%	0·049%
Free fatty acids (as oleic) in secondary extract	50·99%	53·80%	64·00%	74·20%
Unsaponifiables in secondary extracts	33·52%	36·22%	31·00%	—

The unsaponifiable matter in each secondary extract was determined by boiling the fat, under reflux, for 3 hours with 25 ml. of N/1 alcoholic caustic potash, driving off the alcohol and taking up the residue in water. The aqueous solution was extracted three times with diethyl ether and the bulked ether-extracts washed with distilled water until no longer alkaline to phenol phthalein. The ether was evaporated to obtain the unsaponifiables

The unsaponifiables in the secondary petroleum ether extract were not determined, due to the very small amount of fat available

A second set of extractions was later carried out in exactly the same way but using a 60s quality wool top combed in Class "A" Control Oil, and substituting acetone for dichloroethylene These results were as follows —

Table VII

	Acetone	Chloroform	Diethyl ether	Petroleum ether
Initial extract . .	4 098%	4·090%	3 661%	3 566%
Free fatty acids (as oleic) in extract	6 94%	6 96%	3 41%	1 72%
Unsaponifiables in extract	16 10%	15 89%	13 38%	12 90%
Secondary extract . .	0 134%	0 143%	0 064%	0·049%
Free fatty acids (as oleic) in secondary extract ..	52 20%	59 18%	60 85%	87 00%
Unsaponifiables in secondary extract . .	37·77%	35 79%	28 25%	—

These results are extremely interesting and significant. In the first place, in both sets of results the percentages of the individual initial extracts are seen to be in roughly the same ratio as those shown in Tables I and II. The percentages of free fatty acids also vary in a similar manner.

The secondary extracts are more important, however. They are seen to consist largely of free fatty acids, which is reasonable confirmation of the hypothesis that they arise from hydrolysis of the soap residues. Equally important, however, is the fact that the secondary extracts contain quite large proportions of unsaponifiable matter. This substance, although not chemically examined, had the physical characteristics similar to unsaponifiable matter derived from wool fat—*i e* the wool fat alcohols

It will be noted that the free fatty acids and unsaponifiable matter in each secondary extract together total well over 80 per cent Most of the unsaponifiables, therefore, must be present in the secondary extract as free alcohols, with only a small proportion combined as esters This is made even more certain by the fact that the actual percentages of free fatty acids must be higher than the calculated ones shown, these having been determined by titration with standard alcoholic potash and calculated as oleic acid (molecular weight 282) Since a rough estimation of the mean molecular weight of the actual acids has shown it to be well over 300, the figures as oleic are below the theoretical ones.

The existence of these alcohols in the secondary extract is not very surprising Most wool fat derivatives have a strong affinity for other fats and soaps, and it is a difficult matter to separate a mixture of wool fat and fatty acids quantitatively. In the case above, the wool fat alcohols must be contained in the soap residues by virtue of a mutual affinity, and when some fatty acids are removed by a combination of hydrolysis and extraction they carry with them a proportion of the alcohols

With regard to the initial extracts from the wool, it is seen from Table VII that acetone and chloroform (and presumably dichloroethylene also) each extract a larger amount of unsaponifiable matter from the wool than diethyl or petroleum ethers This may be explained by the correspondingly larger content of free fatty acids in both the acetone—and the chloroform—extract These free fatty acids have been presumably hydrolysed and extracted from the soap residues, and have brought with them some entrained wool fat alcohols, thus raising the total contents of unsaponifiable matter in the extracts in question In this case it should be noted that the extracts contain the residual wool fat from the wool, which itself yields unsaponifiable matter (roughly 50 per cent by weight) during saponification of the extracts

From all the results obtained so far, out of the five solvents tested, petroleum ether is apparently the one which causes least hydrolysis of the soap residues during preliminary extraction of the true fatty matters. The next best solvent from this point of view is diethyl ether, whilst dichloroethylene, chloroform and acetone all cause a larger degree of hydrolysis. A final choice as to the most suitable solvent is, however, given later in the article.

With regard to the hydrolysis which takes place, since all the solvents used were carefully dried beforehand, the source of the trouble is indicated to be the natural moisture present in the wool samples.

This is confirmed by the earlier work of Ryberg, who extracted, by means of ethyl ether, the fatty matter from two samples of a scoured wool. One sample was extracted at normal condition, *i.e* , roughly 14·5 per cent moisture content, whilst the other sample was oven-dried before extraction On the average he found that an oven-dried wool sample gave about 0·1 per cent smaller extract than one at normal condition, which is in accordance with hydrolysis being eliminated or largely reduced by the oven-drying.

Even should this be so, however, drying before extraction can hardly be recommended for general work, since it is bound to cause some oxidation of the fats on the wool, especially where an oxidisable combing oil is present. Other means of drying a wool sample, such as by vacuum and desiccants at room temperature would be a long and inconvenient process, and it seems as though for general working a small amount of hydrolysis must be endured, being minimised by the use of anhydrous solvents

Soap Residues

Some discussion of these has already taken place, and from the literature quoted it can be seen that considerable work has already been devoted to them by the workers mentioned.

The proportion of these residues on wool can be quite considerable, and is usually higher than the percentage of residual wool fat. Various estimates of the limits of the percentages of soap found have been given, usually of the order of 0·75 to 1 0 per cent.

The present authors, however, from a large number of tests, have found that the soap residues can lie between 0 4 to 1 3 per cent on a wool top or scoured wool without undue difficulty being encountered in processing Of course, residues as high as 1·3 per cent. are comparatively rare, and, as quoted above, 0·75 to 1·0 per cent is probably the average figure

With a raw wool, there is a comparatively very large proportion of alcohol-soluble matter, this being anything up to 3 or 4 per cent. Most of this matter is removed, however, during scouring of the wool

In order to determine the full extent of the effect of the soap residues upon the estimation of fatty matter, the experiments quoted in Tables VI and VII were taken a stage further The wool samples used in these tests, after being dried of solvent, were each extracted by means of absolute alcohol in the Soxhlet apparatus for 5 hours.

In the case of Table IX, the extracts, after weighing, were re-dissolved in neutral alcohol and free fatty acids determined by titration with N/10 alcoholic potash, against phenol phthalein. The alcohol was evaporated off and the residues dissolved in distilled water A little sulphuric acid was added and each boiled for a few minutes until the soaps appeared to be completely split out, as judged by the clarity of the aqueous and greasy layers. After washing the solutions into separating funnels, the aqueous layers were thoroughly extracted by ether, the latter being then washed several times with water and finally evaporated to recover the fats These recovered fats were submitted to further examination, as shown below

In the case of Table VIII, the alcoholic extracts were not examined beyond determinations of their respective contents of free fatty acids

Table VIII (continued from Table VI)

	Wool previously extracted with			
	Dichloro-ethylene	Chloroform	Diethyl ether	Petroleum ether
Total alcoholic extract	0·749%	0·584%	0·858%	1·022%
Free fatty acids (as oleic) in extract	5·27%	3·56%	3·81%	8·22%

Table IX (continued from Table VII)

	Wool previously extracted with			
	Acetone	Chloroform	Diethyl ether	Petroleum ether
Total alcoholic extract	0·625%	0·474%	0·893%	1·108%
Free fatty acids (as oleic) in extract .	4·59%	5·31%	5·00%	7·77%
Total fats isolated from extract by H_2SO_4	72·23%	75·42%	86·04%	83·00%
Free fatty acids in isolated fats (as oleic) . . .	52·41%	49·90%	50·24%	58·35%
Unsaponifiables in isolated fats	27·00%	28·43%	33·90%	22·25%
Neutralisation value of isolated fats	104	99	100	116
Saponification value of isolated fats . . .	140	132	125	149

These results agree very well with the tables of which they are continuations. It is seen that the amount of alcoholic extract has a rough inverse relation to the amount of true fatty matter extracted at the start. There is also seen to be an excess of fatty acid in the soap over the alkali present. This fact has, of course, been noted by many previous workers, who have attributed it to hydrolysis, in part, of the soap during extraction, the alkali having an affinity for the wool (or *vice versa*) and being retained by it.

As was found by Ryberg, the soap residues contain quite considerable amounts of unsaponifiable matter, which, after all, is only to be expected after finding unsaponifiables in the soap hydrolysis products That some of this unsaponifiable matter, presumed to be wool fat alcohols, is present in the soap residues combined as esters, is indicated by the differences between the neutralisation and saponification values. It should be noted, however, that some of these differences might be accounted for by the presence of lactones in the fatty acids. These are prevalent in wool fat[9,10] and are not affected by cold alcoholic potash They are, however, broken down during the saponification process and form soaps, thus being represented in the saponification value, but not in the neutralisation value

In the instance of the petroleum ether, the ratio of fatty acids to unsaponifiables in the recovered fats from the soap is relatively high, which is a confirmation of the non-extraction by petroleum ether of oxidised or some other type of fatty acids These remain in the soap residues and are extracted later by alcohol.

It has been stated by various workers that some of the soap residues were soluble in diethyl ether, and that extraction by the latter did not, therefore, yield a true figure for the total fatty matter Over several tests, however, the present authors have failed to detect more than a trace of actual soap in a fat extracted by diethyl ether There are, of course, the hydrolysed fatty acids from the soap, and these make a subsequent alcohol extract correspondingly smaller. It seems likely that a misinterpretation of this phenomenon has given rise to the above-mentioned belief that actual soap was extracted.

With regard to the alkali portion of the soap residues, a typical sample of such residues obtained after initial extraction by diethyl ether was ignited and 12·50 per cent of ash thereby obtained This ash was analysed, with the following results:—

Silica (SiO_2)	2 97%
Iron, Aluminium, etc. (as oxides)	1 49%
Calcium (CaO)	2·71%
Magnesium (MgO)	0 49%
Potassium (K_2O)	5 07%
Sulphates (SO_3)	5·94%
Chlorides (Cl)	trace
Sodium (Na_2O, by difference)	81·33%

The soap is indicated from the above to consist largely of sodium salts, with only a relatively small content of potash and other metals. The exact origin of the soaps has not been pursued in this work, but they are believed to be natural soaps derived from the wool grease. The fatty acids, at any rate, bear no resemblance to those of the soaps used in scouring the wool

Soaps Insoluble in Alcohol

As will have been gathered from the literature quoted at the beginning of the article, some of the soap residues are not extracted by alcohol. Processes involving acidification and a second extraction were suggested for removing these.

Accordingly, in order to carry this work to completion, further tests were made on the wool samples already extracted with solvents and alcohol

The wools, after drying free from alcohol were immersed for two minutes in boiling 2 per cent. hydrochloric acid, rinsed, wrung out and air-dried. Each sample was then extracted with a mixture of 85 ml diethyl ether and 35 ml. absolute alcohol for four hours The results are shown below.

Table X (continued from Table VIII)

	Wool previously extracted by alcohol and			
	Dichloro-ethylene	Chloroform	Diethyl ether	Petroleum ether
Total matter extracted by ether/alcohol	0·251%	0 167%	0·220%	0 296%
Free fatty acids (as oleic) in extract	47·35%	68 02%	54 43%	32 41%

Table XI (continued from Table IX)

	Wool previously extracted by alcohol and			
	Acetone	Chloroform	Diethyl ether	Petroleum ether
Total matter extracted by ether/alcohol	0·329%	0·252%	0·224%	0·203%
Free fatty acids (as oleic) in extract	51·13%	44·63%	63·19%	62·37%
Unsaponifiables in extract	12·16%	16·36%	14·13%	5·61%

A quite appreciable amount of some substance is thus left on the wool, even after treatment with both a fat solvent and alcohol.

As to the composition of this matter, no definite opinions can be formed on the above evidence alone. The free fatty acids and unsaponifiables estimated in it do not add up to anywhere near 100 per cent., and even assuming the unsaponifiables to be originally esterified with an equal weight of fatty acid (as in wool fat) there is still a large discrepancy.

The most likely explanation is that the fatty acids are either of high molecular weight or are composed largely of lactones or inner anhydrides.

It is a matter of some interest that even in these last traces of soap left on the wool a proportion of unsaponifiable matter is still found. This demonstrates the truly remarkable affinity between wool fat compounds and other fatty bodies.

Later work than the above has shown that these soap residues, classed as being insoluble in alcohol, are actually soluble to a small extent, or, at any rate, their hydrolysis products are.

A sample taken from a normal wool top, scoured with soap and alkali and combed in Class "A" Control Oil, was extracted with diethyl ether for 3 hours. It was then subjected to extraction with absolute alcohol, the extracted matter being isolated and weighed after definite intervals:—

	After 2 hours	After 4 hours	After 6 hours	After 8 hours
Total alcoholic extract	1·14%	1·25%	1·31%	1·37%

It is apparent that small quantities of some substance are being extracted, even after 8 hours extraction with alcohol.

As a further test, two more samples of the same wool top were de-fatted with diethyl ether and extracted with alcohol for 5 hours. One sample only was then immersed for 2 minutes in boiling 2 per cent. hydrochloric acid, rinsed, squeezed and air dried, both samples being finally extracted for 4 hours with a mixture of 85 ml. ether and 35 ml. alcohol. The following results were obtained.

	Final ether/alcohol extract	Free fatty acids (as oleic) in extract
Acid-treated wool	0·191%	52·29%
Untreated wool	0·125%	34·17%

A large proportion of the residue is thus seen to be obtainable without a preliminary acid-treatment. Seemingly, if an alcohol-extraction were carried on long enough all these last traces of soap would be removed (largely as hydrolysed fatty acids) without an acid-treatment, but this treatment speeds up their removal. What seems definite is that they should be included in an estimation of the total soap residues, since they clearly belong to this class of impurity

Summary and Conclusions

The impurities generally found in wool may now be enumerated in greater detail:—

(*a*) (1) Wool fat esters, free fatty acids and free wool fat alcohols
  (2) Added oil;
(*b*) Soaps soluble in alcohol, with entrained wool fat derivatives,
(*c*) Soaps almost insoluble in alcohol, with entrained wool fat derivatives

Most of the group (*a*) bodies can be removed by treatment with a suitable solvent. Some of the wool fat alcohols and a smaller amount of the esters, however, are retained on the wool by reason of an affinity between them and the soap residues. Also, during extraction of fats of group (*a*) some hydrolysis of the soap residues occurs, and the hydrolysed fatty acids are simultaneously extracted, bringing with them a further small amount of wool fat esters and alcohols

By subsequent treatment with alcohol group (*b*) soaps are extracted, there being entrained and extracted with them a considerable proportion of wool fat alcohols and some esters During extraction, hydrolysis of these soaps continues, the alkali portion being retained by the wool and the extracted soaps thus containing an excess of fatty acid portion

To extract the remaining group (*c*) soaps from the wool, a treatment with acid as previously described is recommended, followed by further extraction with an ether/alcohol mixture. These soaps, or rather fatty acids, contain what are presumably the last traces of wool fat derivatives which were on the wool

The extraction of fatty bodies from wool is seen from the foregoing to be extremely complicated. No clear cut separation of all the various substances can be obtained due to strong mutual affinities The most that can be done, apparently, in general work is to classify the substances into three somewhat arbitrary groups.

(*a*) True fatty matter, solvent extracted,
(*b*) Soap residues, *etc* , alcohol-extracted;
(*c*) Insoluble soap residues, *etc* , ether/alcohol-extracted

These three estimations will give a useful knowledge of the state of the wool and, of course, in special cases, further information can be obtained by more detailed examination of the three extracts

Choice of Solvent: Summary

On the whole, the most generally satisfactory solvent for the initial extraction of fatty matter is indicated to be diethyl ether Petroleum ether must be discarded due to non-extraction of certain of the fatty acid components of wool fat, whilst acetone, dichloroethylene and chloroform all appear to cause a greater degree of hydrolysis of the soap residues than does diethyl ether.

King[1] stated that petroleum ether extracts notable quantities of soap, but this would not appear to be the case from the results of the present work, the soap residues estimated after preliminary extraction with petroleum ether being larger in amount than those resulting from the use of any other solvent tested. Whether or not soaps are extracted, however, the merits of petroleum ether do not outweigh those of diethyl ether, which has been shown not to extract appreciable amounts of soap as such.

In addition to the above work some short tests were made using benzene, but this appears to offer no advantage over any of the other solvents, and suffers from the disadvantage of being difficult to boil sufficiently rapidly for use in a Soxhlet apparatus on a steam bath.

The ether used should, of course, be anhydrous and free from alcohol so as to cut down any soap hydrolysis to a minimum. Comparative experiments have been carried out by the authors using dry ether and ether containing varying amounts of water, and it was found that the water content had a pronounced effect, in extreme cases causing over 0·2 per cent error in the fatty matter extracted For the estimation of group (*b*) substances the use of absolute alcohol seems to be generally established, while for extraction of group (*c*) the authors prefer the use of a mixture of diethyl ether and absolute alcohol in a ratio of 85/35. The preference for this mixture is to ensure extraction of acids which might only be soluble in one of the two liquids

The grade of diethyl ether used in general work has the following specification —

Boiling range—34-36° C
Specific gravity—0 720-0 724/15 5° C.
Non-volatile matter—Not more than 0·002 per cent.
Moisture—Not more than 0 05 per cent.

General Remarks

The use of corks as opposed to ground glass joints has been shown by King to be unsatisfactory Apart from possible leakage or contamination of the corks due to their porous nature they were shown to contain some matter which is ether-soluble, leading to erroneous results when used for the purpose in question.

In order to get reproducibility and uniformity of results, it is desirable that standards should be fixed for all such points as above, including sizes of apparatus and sample, time and rate of extraction, purity of solvent and items of general procedure, such as drying of the residue and whether or not thimbles are used during the extraction.

On the whole, there seems to be no serious reason why such standards should not be evolved and applied universally, so as to make the method uniform throughout the textile trade and profession.

The Commercial Scour Test

This has been mentioned before as being still widely employed in the trade for the estimation of fatty matters on wool

Its principle, it may be briefly mentioned, is to weigh a quantity of wool, usually 8 ozs , at natural condition and again in a bone-dry state. The wool is then scoured by hand in a series of wash-bowls (usually two), finally rinsed in a third bowl of clean water and then weighed again bone-dry The difference in weight or loss between the two bone-dry weighings is calculated as a percentage and termed "Fatty Matters, *etc* "

There are no generally recognised standards for the compositions of the detergent liquors, although individual workers may have their own standard working particulars It is often considered sufficient merely to have a reasonable excess of detergents present, without accurately weighing them. The method is recognised as giving results which differ to a somewhat variable extent from those of the ether-extraction method, and it was considered desirable to include in the present investigation some comparison between the two methods

The standard procedure adopted for the scouring tests herein described was as follows:—

No 1 Bowl 20 gm best potash-olive soap } dissolved in 5 litres
8 gm anhydrous sodium carbonate } water
5 minutes immersion at 120°F.
No. 2 Bowl 8 gm soap } dissolved in 5 litres water
3 gm sodium carbonate }
3 minutes immersion at 115-120°F.
No 3 Bowl Clean water rinse.
3 minutes immersion at 110°F.

Some normal wool tops were taken and the individual Gross Scour Losses determined. Diethyl ether-extractions were carried out on duplicate samples, followed by determination of the respective alcohol-solubles. The results are shown below, the tops in this case all being combed in B M (Blended Mineral) Oil.

Table XII

	Sample Number			
	1	2	3	4
Gross Scour Loss (Fatty matters, etc)	3·363%	3·130%	3·525%	3·016%
Fatty matter (ether-extracted)	4·040%	3·596%	4·028%	3·615%
Alcohol-soluble matter ...	1·182%	1·290%	1·266%	1·291%

The Gross Scour Loss is in every case much smaller than the ether-extracted fatty matter.

A similar set of results was obtained by carrying out further trials on wool tops which had been combed in Class "A" Control Oil:—

Table XIII

	Sample Number			
	1	2	3	4
Gross Scour Loss . . .	3·220%	3·443%	3·517%	3·099%
Fatty matter (ether extracted) . . .	3·422%	3·545%	3·810%	3·463%
Alcohol-soluble matter . .	0·808%	0·733%	1·020%	1·035%

Here again the Gross Scour Losses are well below the ether extractions, but to a smaller extent.

It is desirable to add here, that the above figures do not form the only evidence of this discrepancy Many other results have been obtained from time to time which have practically all shown the same effect, although in some cases the methods showed good agreement Even during the period when olive oil was in general use by woolcombers, no satisfactorily consistent agreement was obtained.

In an attempt to shed light on the source of this discrepancy a 64s quality wool top, combed in B M. (Blended Mineral) Oil was submitted to a Commercial Scour Test. The resulting scoured sliver was then ether-extracted under the standard conditions and finally alcohol-extracted. Ether- and alcohol-extractions were also carried out on a sample of the original top in oil.

It is seen that a considerable proportion of ether-soluble matter remains on wool after being treated by the Commercial Scour Test What is more, the proportion of alcohol-solubles has actually been increased by the treatment.

	Scoured Top	Original Top
Gross Scour Loss . .	3·010%	—
Ether extract	0·412%	3·612%
Alcohol extract	1·106%	0·817%
Total	4·528%	4·429%

The ether extract obtained from the scoured wool top was examined and gave the following results:—

Free fatty acids (as oleic)	56·79 per cent
Unsaponifiables .	25·31 per cent
Melting point . .	28·0° C.

It is thus seen to consist of roughly half free fatty acids, and on these grounds appears similar to the secondary ether extracts analysed in Table VI, *i.e.*, it appears to be largely a hydrolysation product of soap residues. The amount, however (0·4 per cent.), is more than would be expected from a normal soap residue, at any rate so far as previous results have shown, and indicates the possibility that soaps are absorbed from the detergent liquors by the wool during testing. This is borne out by the overall increase in alcohol soluble matter.

Another point of interest is the comparatively low melting point of the ether extract. This may be owing to its containing a small percentage of added oil which was not removed during the Commercial Scour Test (possibly due to an affinity between the added oil and other fatty matter).

In view of the results obtained from this preliminary work, a more detailed set of experiments was subsequently undertaken.

Results have been given in previous tables that were obtained by subjection of wool successively to initial diethyl ether-extraction, secondary ether-extraction, alcohol-extraction, acid treatment and a final ether/alcohol extraction. The same lot of wool as was used to obtain those results was now subjected to a Commercial Scour Test, followed by a diethyl ether-extraction, alcohol-extraction and the rest of the sequence above, with examination of all the extracts obtained. The results are given below. For ease of comparison the corresponding results obtained on the original non-scoured wool top are re-quoted alongside.

In the first place it is noted that the total matter extracted from the scoured top is over 0·5 per cent. greater than that from the original. Although some of this difference will be accounted for by the removal of non-fatty matter (such as dust, portions of fibre, *etc.*) during the Commercial Scour Test, it can be seen from the tables that most of the difference lies in the matter afterwards extracted by solvents. Moreover, soaps or their hydrolysed fatty acids are, in the main, responsible for the discrepancy. These are present in considerably greater amounts than before scouring, and obviously deposition of them on the wool has taken place during scouring. These extra soaps retain in them the usual proportion of wool fat alcohols or esters, thus accounting for smaller removal of true fatty matter during the Commercial Scour Test than during ether-extraction.

In the wool tested here, the Gross Scour Loss is not very far below the ether extract, but it should be noted that not all of this loss on scouring is fatty matter. Non-fatty matters such as solid dirt, dust, *etc.*, are also included in such a figure. This fact is generally recognised, however, and where a more accurate estimation of the net fatty matters on wool is desired by the Commercial Scour Test, a separate estimation of these non-fatty impurities, commonly designated "Insolubles", is made and deducted from the total Gross Scour Loss.

	Top tested by the Commercial Scour Test	Top tested by diethyl ether-extraction
Total fatty matter (Gross Scour Loss)	3 590%	—
Total fatty matter (Diethyl ether extracted)	—	3 661%
Subsequent diethyl ether extract	0 288%	0 064%
Free fatty acids (as oleic) in ether extract	61 30%	60 85%
Unsaponifiables in ether extract .	14 95%	28 25%
Alcohol extract . .	1 108%	0 893%
Free fatty acids (as oleic) in extract	6 97%	5 00%
Fatty matter split out by H_2SO_4	82 85%	86 04%
Free fatty acids (as oleic) in split-out fats .	52 85%	50 24%
Unsaponfiables in split-out fats . . .	18 63%	23 90%
Neutralisation value of split-out fats	105	100
Saponification value of split-out fats	155	125
Ether/alcohol extract after acidification	0 398%	0 220%
Free fatty acids (as oleic) in extract .	38 78%	63 19%
Unsaponifiables in extract . .	32 42%	14 13%
Total matter extracted from wool	5 384%	4 838%

This is not a necessarily accurate procedure, since the insolubles removed by a special test might not be the same as those removed during an actual Commercial Scour Test.

On the whole, it seems that the Commercial Scour Test is inferior in accuracy to the ether extraction method There is less efficient removal of fatty matters due to greater retention of them in the increased soap residues, and this increase in soap is itself a serious source of error, probably being the main reason for the low results characteristic of the Commercial Scour Test In addition, the occurrence of variations due to non-uniform handling by the operator is not a very remote possibility. The method is certainly no quicker than an ether extraction, and has not the same adaptability to the different forms of wool encountered at the various stages of processing What may be its sole advantage is that a larger sample is employed, reducing possible error due to non-uniform distribution of fats on the wool, but where results to which importance is attached are desired, it seems that the Commercial Scour Test should yield place to an ether-extraction performed under standard conditions

REFERENCES

[1] Woodmansey *J Soc Dyers & Col*, 1919 35, p. 169,
[2] Hummel "Organic Analysis," Allen, 8, p 682
[3] Maercker & Schulz "Methods of Textile Chemistry," Dannerth, p 60.
[4] King *J Text Inst*, 1922 13, p T143, (also W I R A Publication No 16).
[5] Trotman "Textile Analysis," 1932. p 160,
[6] Gilmore *Amer Dyes Rep*, 1934 23, p 642,
[7] Von Bergen *Amer Dyes Rep*, 1937 26, p 314,
[8] Ryberg *Amer Dyes Rep.*, 1937 26, p 461,
[9] Lower *Oil & Col Trades J*, 1948 2596, p 150,
[10] Lewkowitsch "The Technology and Analysis of Oils, Fats and Waxes," 1921, 2, p 904

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Woolcombers Limited,
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22—TORQUE-TWIST RELATIONSHIPS IN SINGLE AND MULTIPLE RAYON FILAMENTS

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The stress-strain behaviour of textile fibres under tension has been the subject of study by numerous workers over a considerable period, and the characteristic shapes of the curves for a wide range of materials are now matters of common knowledge. In the case of regenerated rayons in particular, the approximate locations of the so-called yield points have been established, so that the users of these materials may know the limits of stress and strain which should not be exceeded if various undesirable consequences are to be avoided. Up to the present time, however, no corresponding information has been available in respect to the behaviour of fibres in torsion. Their immediate reactions to very small strains have been measured by means of the torsion-pendulum test, but the results of such tests are completely inadequate for predicting or explaining the behaviour of fibres when subjected to the torsional strains commonly applied in practice. The present paper records the results of experiments carried out on certain rayon materials in order to remedy this deficiency.

Materials

The materials examined were chosen from a varied selection of commercial yarns kindly supplied by Messrs. Courtaulds Ltd., and British Nylon Spinners, Ltd., in 1944. Those used in the experiments are listed in Table I, together with their nominal particulars.

Table I

Sample No.	Material	Yarn denier	No. of filaments	Filament denier
1	Viscose " Bright ". .	60	16	3·75
1b	" "	100	21	4·75
2	Tenasco	60	20	3·0
4	Acetate " Natural "	75	20	3·75
7	Nylon	45	15	3·0

Photomicrographs of transverse sections showed that all the samples were reasonably uniform in filament shape and dimensions, except in the case of Tenasco where the filament denier appeared to vary considerably. The deviations of the different samples from the ideal cylindrical shape have of course to be taken into account in any comparison of absolute torque values.

As received, the materials were in the form of slightly twisted yarn on pirn. In order to secure similar initial conditions in all samples it was considered necessary to bring them all into a common unstrained state by a pre-treatment designed to release strains developed during the manufacturing processes. Samples of yarn about 40 cm. long were first completely untwisted in a twist-tester and the individual filaments carefully separated with a dissecting needle before being fastened down at each end to a small piece of adhesive plaster. The bands of parallel filaments were next transferred to a specially made frame having string sides shorter in length than the filaments themselves so that when the whole was hanging freely the specimens were free to contract under no greater load than that of their own weight. The charged frame was then immersed in water at 30° C. for about 10 minutes, after which it was transferred to a drying oven at 103° C. for a period of at least 48 hours. On removal from the oven, the samples were stored until required in a large desiccator containing calcium chloride, so that when finally conditioned before testing, all specimens reached equilibrium with the atmosphere from the dry side

All the experiments described in the present paper were carried out on specimens in equilibrium with an atmosphere of 65 ± 2 per cent R.H at a temperature of 20 ± 1° C

Experimental Method

The instrument employed and the manner of its use have already been described.[1] In brief, the apparatus comprises five independent torsiometers, each consisting essentially of three main parts arranged in vertical alignment, at the top a measuring head, at the bottom a twisting unit, and between them a rigid connecting link carrying an equilibrium pointer The connecting link and equilibrium pointer are suspended from the rotatable measuring head by a calibrated phosphor-bronze torsion wire of known length and appropriate characteristics The specimen in turn is suspended from the connecting link and carries at its lower end a small tension weight and light torsion bar engaging with vertical prongs mounted on the twisting unit which is rotated at a uniform speed by a small electric motor fitted with a reduction gear. The twist thus imparted to the specimen generates a progressively increasing torque which is balanced by manual counter-rotation of the measuring head, the equilibrium pointer being maintained steadily in position throughout the process The angular displacement of the upper end of the torsion wire corresponding to the amount of twist in the specimen is noted at suitable intervals, and thence, from the calibration constant for the wire in use, the torque at various twists may be calculated.

The experiments here reported fell into two groups: (*a*) those on single filaments of the five materials listed in Table I, and (*b*) those on multiple-filament specimens of sample No 1, Viscose of 3·75 filament denier In all cases, five specimens 10 cm. in length were taken from the pre-treated samples already mentioned and mounted in the five units of the torsiometer cabinet, where they were conditioned overnight before being tested at a straining rate of 10 turns per cm per minute The test ended when the contraction of the specimen raised the bottom torsion bar out of control of the prongs of the twisting unit, whereupon the specimen swung free It is thought that at this stage the condition of the specimen cannot have been far short of rupture

As already noted, the readings taken were those of θ, the angular rotation of the upper end of the torsion wire To convert these into net torque, *i e* torque arising solely from the applied torsional strain, it was necessary not only to make the obvious corrections for any small differences in length of the phosphor-bronze wire used in the different units, but also to make allowance for the untwisting couple due to the suspension weight The latter was determined from the energy required to lift the weight through the distance by which the sample contracted To this end, the shortening of similar specimens as twist increased was measured with a cathetometer and the relationship between the two quantities plotted The area under the curve was then measured with a planimeter and the amount of torsional energy absorbed by lifting the suspension weight calculated This energy subtracted from the total energy (area under the torque/twist curve representing the raw data) gave the net energy used solely in twisting the specimen

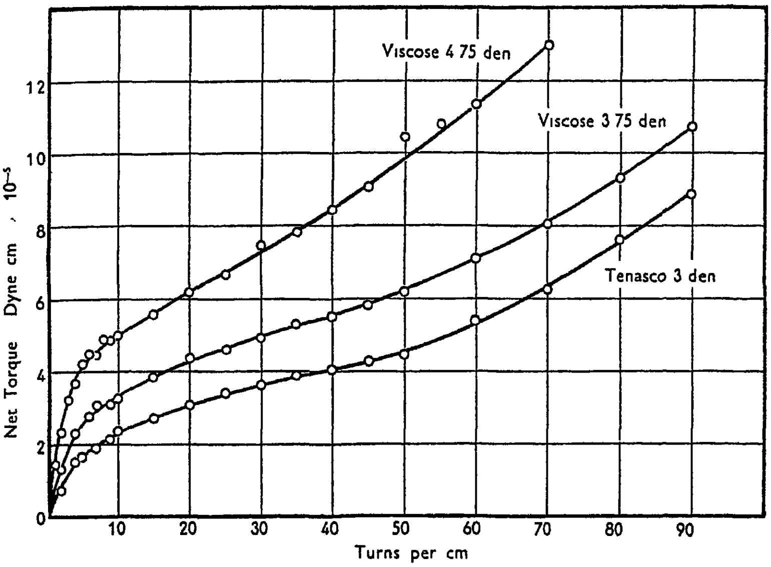


Fig 1

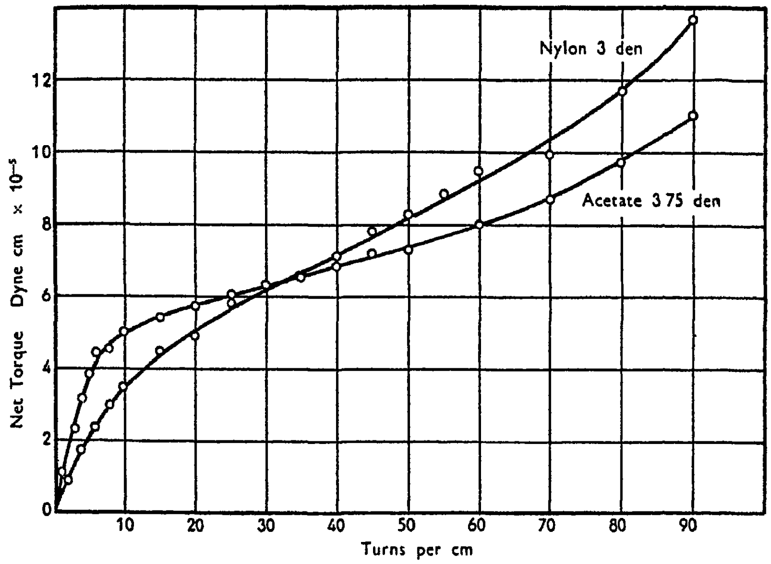


Fig. 2

Results for Single Filaments

The results obtained in the manner described are most conveniently presented in the form of graphs, and these are given in Figs. 1 and 2 for the different materials examined. In addition Table II, which refers to Viscose 3·75 denier, is given to show how the five different specimens varied among themselves. The differences were not large, and similar conditions prevailed with the other samples. Each graph refers to the specimen chosen as most closely representing the average behaviour of the five.

Table II

Diam of phosphor-bronze wire =0 00254 cm
Suspension weight =0 175 gm.
Rate of twisting =10 turns/cm /min
Material Viscose filament 3 75 den

Turns per cm *	Torque, dynes cm. × 10^{-5}				
	Test 1B 1	Test 1B 2	Test 1B . 3	Test 1B 4	Test 1B 5
2	1 34	1 54	1 39	1 36	1·28
4	2 36	2 48	2 32	2 19	2 22
6	2 78	3 08	2 66	3·10	—
8	3 09	3 39	2 99	3 31	2 86
10	3 35	3 55	3 20	—	3 17
15	3 92	4 37	3·78	4 17	3 81
20	4·38	4 52	4 15	4 59	4 18
25	4 61	4 96	4 45	5·04	4 45
30	4 95	5 33	4 75	5 32	4·72
35	5 32	5 65	5 05	5 81	5 36
40	5 55	5 90	5 42	5 92	—
45	5 83	6·22	5 72	6 26	5 60
50	6·21	6 56	6 08	6 75	6·07
60	7 17	7 00	7·14	7 65	6·57
70	8 08	8 32	—	8 70	7·48
80	9 37	9 26	—	10 26	9·10
90	10 75	10 93	—	11 48	10·44

* Based on the initial length of the specimen

It will be seen that these torque/twist curves were characterised by a sigmoidal shape similar to that exhibited by the more familiar load/elongation plots. In all cases save that of nylon, three more or less distinct regions or sections are apparent —An initial section, which in general can be regarded as a non-Hookean elastic range; eventually breaking down by yielding to a section where great changes of strain are accompanied by small changes of stress, and finally succeeded by a strain-hardening region where the reverse effect takes place For the ordinary viscose and acetate samples the yield range, apparently occurring in the region of 6 to 10 turns per cm , is most pronounced, while in Tenasco it is not nearly so marked In the curve for nylon on the other hand, there is no obvious indication that yield takes place at all.

In reference to longitudinal tests, the interpretation of the corresponding three phases of behaviour which finds current acceptance may be briefly summarised as follows —

The general deformational properties of a material are ultimately determined by the balancing of externally applied forces by the reaction of the internal forces inherent in its molecular structure, and the nature, magnitude and distribution of these intra- and inter-molecular forces decide the pattern and stability of the whole molecular network The three-dimensional network of a textile substance consists of long-chain molecules which in parts, owing to proximity and mutual parallelism, form regions of high geometric order (crystalline regions), but which elsewhere, not being in such a favourable position for strong interaction, are only randomly held and so form regions of partial molecular disorder (amorphous regions)

The process of deformation of such a system is imagined to consist of the following phases·—

On application of stress, potential energy is stored up by the extending or shearing of secondary and/or primary bonds This elastic deformation is associated with the displacement of the atoms from their position of equilibrium in the potential trough On removal of stress, the atoms fall back and regain their initial state of equilibrium, and complete recovery takes place This elastic deformation, the nature and magnitude of which depends on the molecular constitution, will occur mainly in the amorphous fringes.

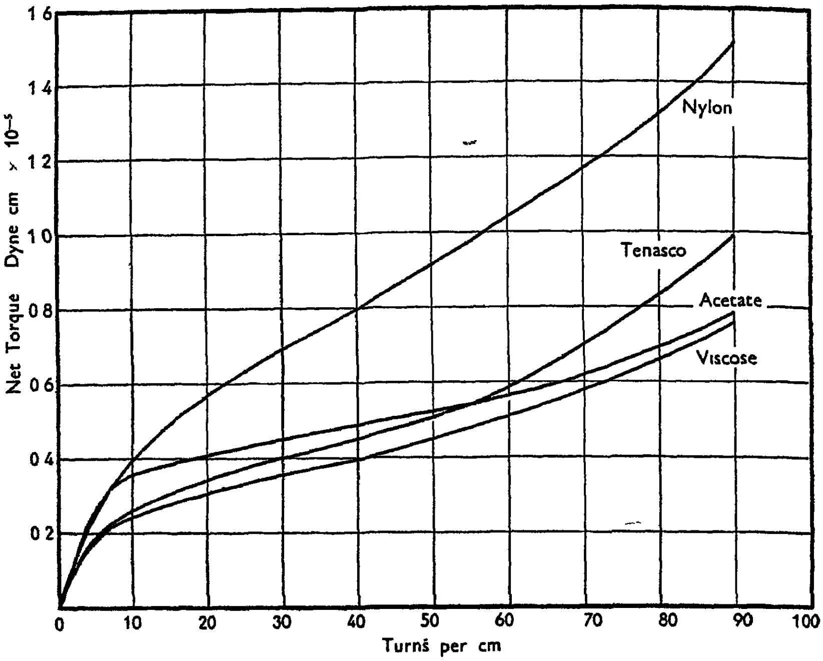
As the strain increases, however, thermal agitation causes an increasing number of atoms to jump over their potential barriers and find new positions of equilibrium, thus giving rise to the initial stages of structural rearrangement With the breaking of secondary bonds, partial lengths of the molecular chain will be freed and their energy will be used in straightening and aligning these free lengths. There is the added possibility, particularly in materials like wool and nylon, of kinetic elasticity resulting from the contractile tendency of the molecules in striving to return to their natural state of higher entropy or random arrangement.

On further increase of stress, there follows a period of rapid deformation This great increase of strain for relatively small increments of stress has been described as structural viscosity although, for textile materials at least, the use of this term is apt to be misleading because it implies completely irreversible deformation. In this phase, a re-orientation of the whole three-dimensional network takes place which accounts for the greater part of the total deformation This mechanism is possible mainly because of the flexibility of the amorphous fringes which may be imagined as forming the loose joints of the molecular network

Finally, as still higher stresses are imposed, the process of re-orientation results in a structural arrangement better able to withstand stress, and a slowing down of deformation, *i e* strain hardening, takes place.

In the parallel case of torsional relaxation, similar mechanisms may be expected to prevail although the magnitude of their effect will be different, depending on the anisotropy of the material. Although the shearing or extending of secondary bonds can easily be imagined as exactly the same process in torsion as in tension, the process of re-arranging the molecular network, which in a tensile test takes place in the direction of the applied stress, is not so readily visualised in the case of torsional deformation The application of transverse shear forces to a loose and irregularly connected structure will result in a very complex system of tensile and compressive forces acting on the constituent elements, combined with a tendency to form a spiral structure which will produce contraction of the specimen as a whole It seems reasonable to assume that the formation of a spiral structure will induce a closing up of the loose and open molecular network in directions both perpendicular to and along the axis of the filament. In this connection, however, it has to be noted that the intensity of shear at a point varies according to its distance from the torsion axis, and consequently the rearrangement and resultant straining of the inter-molecular bonds will be greatest near the periphery of the filament

For the purpose of comparisons between materials it is therefore necessary to take into account any differences there may be in filament denier For cylindrical isotropic bodies the torque required to produce a given torsional strain varies as the square of the area of cross-section. On the assumption that the same relationship is approximately true for the materials under consideration, the results can be brought on to a comparable basis by dividing the net torque either by the square of the denier, or by the square of the area of cross-section calculated from the denier and the density These two measures will, of course, give different rankings to a range of materials


1 6
1 4
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0 4
0 2
Net Torque Dyne cm × 10⁻⁵
0
10
20
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40
50
60
70
80
90
100
Turns per cm
Nylon
Tenasco
Acetate
Viscose

Fig 3

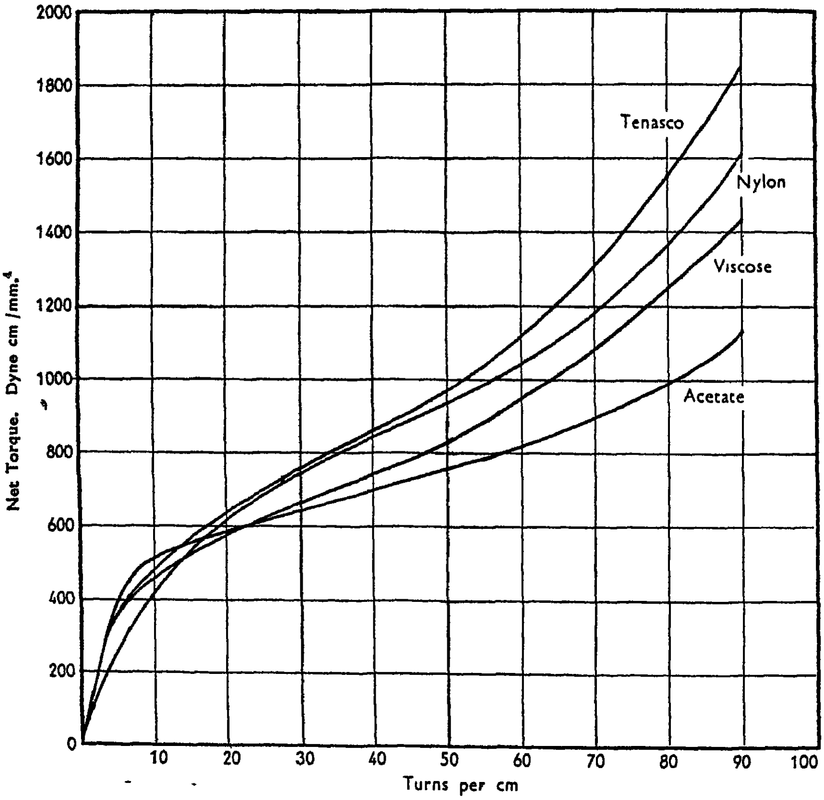
2000
1800
1600
1400
1200
1000
800
600
400
200
0
Net Torque. Dyne cm /mm.⁴
10
20
30
40
50
60
70
80
90
100
Turns per cm
Tenasco
Nylon
Viscose
Acetate

Fig. 4

depending on their densities, and which of the two should be used will be decided by the purpose for which the comparison is required.

In Table III are given the results for the five materials in terms of torque divided by the square of the nominal denier When this adjustment is made, the results for the two viscose materials are almost the same, except at less than 3 turns per cm , wherefore only one plot for Viscose (3·75 den) is shown in Fig 3 When density as well as denier is taken into account (see Fig 4), the two bulkier materials, nylon and acetate, are ranked down relative to the others in the resistance to strain It is interesting to observe from Fig 4 that at low twists the three cellulosic materials gave almost identical results, sharp differentiation being evident only at strains greater than 4 turns per cm. The trends shown by the two plottings are sufficiently clear to require no further description in detail, and call only for the comment that the results of dynamic tests at low strains are evidently far from reliable guides to the torsional behaviour of fibres at the higher strains that are common in industrial practice.

Table III
Net Torque/Cross Sectional Area^2
Dyne cm /mm ^{4}.

Turns/cm	Viscose 3·75 den.	Viscose 4 75 den.	Tenasco 3·00 den.	Acetate 3 75 den	Nylon 3·00 den.
1	84·2	121	80	116	63
2	177	194	153	167	103
3	243	269	251	240	153
4	314	307	316	325	202
5	344	352	342	392	262
6	370	372	363	449	278
7	412	368	395	443	319
8	412	408	427	463	351
9	415	408	440	505	367
10	432	416	477	508	406
15	522	464	566	548	522
20	583	517	638	582	575
25	613	554	707	617	691
30	658	622	756	650	—
35	707	651	804	666	768
40	738	703	842	701	838
45	776	757	888	735	916
50	827	868	926	746	970
60	954	945	1,120	813	1,112
70	1073	1077	1,298	886	1,170
80	1245	—	1,588	995	1,370
90	1430	—	1,848	1,123	1,603

The angular distortion at the surface of the filament, corresponding to the surface angle of twist in a yarn, is also of some interest, and can be readily calculated on the assumption of circular cross-section Such calculated quantities will hold good with considerable accuracy for nylon, but less so for the other materials with their irregular sections Nevertheless they suffice to indicate the general order of magnitude of the surface distortion Table IV shows for each material the diameter it would have if of circular cross-section, and the calculated surface angles corresponding to 5, 10, 40, 70 and 90 turns per cm

The occurrence of yield in torsion as well as in tension assumes a special significance in reference to the distribution of twist in spun rayon yarns As has been shown, the onset of yield in the case of the cellulosic filaments took place when the twist was of the order of 6 to 10 turns per cm , and it is probable that similar results would be obtained for the corresponding staple fibres. Therefore, on any spun rayon yarn of such a count that the average twist is of that order, the fibres in the thick places are likely to be at a strain below the yield strain, while those in the thin places are strained beyond it Under such conditions the disparity in twist between the thick and thin places cannot fail to be accentuated

Table IV

	Viscose 3 75 den	Viscose 4 75 den	Tenasco 3 0 den	Acetate 3 75 den	Nylon 3 0 den
Calculated dia μ .	18 7	21 1	16 7	20 0	19 3
Calculated surface angle at 5 t/cm	1 7°	1 9°	1·5°	1 8°	1 7°
,, ,, ,, ,, 10 t/cm	3 4°	3 8°	3 8°	3 6°	3 5°
,, ,, ,, ,, 40 t/cm	13 2°	14 8°	11 9°	14 1°	13 6°
,, ,, ,, ,, 70 t/cm	22 3°	24 9°	20 2°	23 8°	23 0°
,, ,, ,, ,, 90 t/cm	27 8°	—	25 3°	29 5°	28·6°

Results for Multiple Filament Specimens

Composite specimens of 3·75 filament denier viscose were prepared consisting of 2, 3, 4, 6, 7, 8, 9, 12 and 16 filaments, the latter being the same as the commercial yarn from which the single filaments were withdrawn except that it had no twist. Care was taken in the mounting to ensure that in all cases the lengths of the parallel constituent elements were the same, because uneven lengths of filament could upset the torsional behaviour of the specimens. Torque/twist tests were carried out on at least five specimens in each case, and in Fig. 5 the average values of torque are plotted against turns per cm. for the different numbers of filaments.

The most striking feature of these results is that whereas initially the torsional resistance progressively increases with increasing number of filaments in the specimen, there is a critical number of filaments, namely 7, for which the torque drops sharply, and thereafter the resistance increases again with the number of components The apparently anomalous behaviour of the specimens consisting of 7 filaments is shown by the broken line plot. As can be seen, the torque at low twists falls below that of a specimen consisting of 4 filaments and throughout all twists it remains below that of a 6 filament specimen

When the logarithm of the torque is plotted against number of filaments (Fig 6) a fairly good straight line fit is found for 4 filaments and below, and for 9 filaments and above, while there is a pronounced dip between 6 and 8 The explanation of this behaviour is to be found in the tendency of certain yarn structures to form a core With 1 to 4 components a compact structure is formed with no core, all the components following similar helical paths With 5 components there is a sufficiently large central space to encourage one of them, under the influence of longitudinal tension, to move inwards towards the axis, thus breaking the symmetry of the three-dimensional pattern. With 6 components the tendency is more pronounced, and with seven, the core space is of such a size that its occupation by one of the components is inevitable The addition of the 8th component should theoretically start the formation of a new layer, but especially since we are dealing with filaments that are irregular instead of circular in cross-section, it is more than probable that this component will sometimes tend to compete with the 7th for the core space inside the other six Thereafter, or so it would seem from the present results, the formation of the 3rd zone of filaments proceeds normally

The formation of a core means that any filament which occupies—or goes part way towards occupying—the core position will have a shorter path to follow, and being of the same length as all the others, it will therefore assume a somewhat buckled condition of such a kind as to diminish its torsional resistance about the specimen axis Any such filament, then will make a smaller contribution to the total torque in the specimen than the others which follow a less tortuous path. This would explain the diminished contribution of the fifth and sixth filament, but it still remains to account for the fact that the addition of the seventh filament reduces the total torque to a value lower than that given by six One must therefore suppose that the highly tortuous path followed by the seventh filament in the core position is sufficiently pronounced to disturb also the helical forms of the surrounding six and so to reduce the torsional resistance of these as well

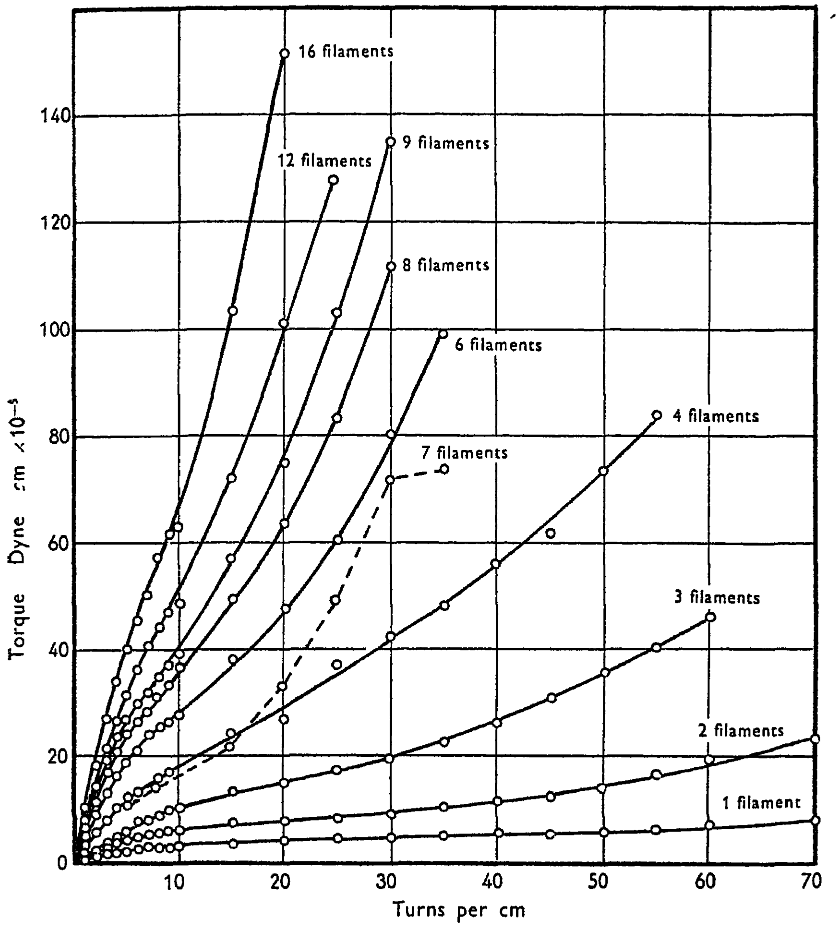

Fig 5

The logarithmic relations which have been noted are, of course, no more than empirical Any twisted composite structure such as we have under consideration must be characterised by a behaviour lying somewhere between two extremes · (i) that of a number of components fitting perfectly together and adhering so that they possess no power of independent movement, in which case the torsional resistance would be proportional to the square of the number of components, and (ii) that of a number of components free to move and rotate in any direction entirely independently of one another In the latter case the torsional resistance would be the sum of the resistances of the individuals. In the limiting condition where the twist is so small that the components could be assumed to be practically straight, the resistance would be directly proportional to their number, but under all other conditions of twist, the linear relationship is modified according to the nature of the paths which the different individuals are constrained to follow A mathematical treatment of torsional strain in "bent strings" has been given by Woods[2] who has shown that, for a helix, the "tortuosity" is given by sin α cos α, where α is the helix angle There would be little profit, however, in attempting to derive a general theoretical expression for the total strain in a twisted aggregate of independent individuals such as are under consideration here In the first place it would be necessary to make the simplifying assumption that all the components follow a helical path, a condition which, as shown above cannot apply to specimens containing more than 4 filaments, and secondly, even though a theoretical lower limit of resistance might be determined there are no means of knowing the extent to which this resistance is in practice augmented by mutual interference among the filaments As regards the latter we can at present do no more than advance the qualitative statements that the interference, and therefore the torsional resistance, will increase with twist for a given number of filaments, will increase with number of filaments for a given twist, and will vary according to the shape and frictional properties of the filaments concerned It can approach but can never reach the condition corresponding to that of a solid rod.

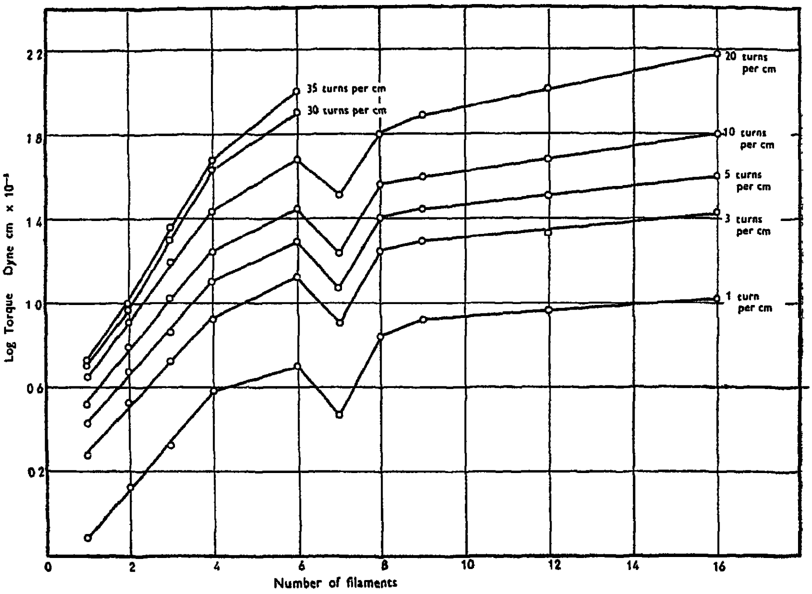

Fig 6

From the foregoing considerations it is evident that fundamental work on the torsional rigidity of textile raw materials must be confined to the most elementary form of specimen, namely, the single straight filament

REFERENCES

[1] Morton and Permanyer *J Text Inst*, 1947, 38, T54
[2] Woods. *J Text Inst*, 1933, 24, T317

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23—FROTH FLOTATION OF FIBRES

By J M Preston and S Saha

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INTRODUCTION

Many processes have been devised for the froth flotation of mineral particles The methods depend on making the surfaces of the particles hydrophobic and aerating an aqueous suspension of them.[1,2,3,4] The methods have been refined so that it has become possible to float selectively particular constituents of a mixture Great use is now made of selective froth flotation in the winning of minerals [5] Flotation methods have also been applied recently to the removal of organic matter from suspensions [6,7] It appeared probable that similar methods could be applied to fibres, and that it should be possible to separate the constituents of a mixture of fibres and to investigate the hydrophobic or hydrophilic behaviour of fibres in aqueous media

The principal methods in present use for the separation and analysis of fibre mixtures are solubility methods,[8] and counting methods [9] There are also a few less used methods depending on density[10] and proximate analysis [11] Many of these methods are quite satisfactory, but some are unsatisfactory or require a high degree of skill In these cases there is scope for improvement. It was thought that froth flotation might prove useful in these difficult cases.

The flotability of fibres was studied at various *pH* values and with the addition of various surface active agents The effects of dyeing and a few other pre-treatments were investigated A broad survey was made of different fibres under these conditions

EXPERIMENTAL

The shapes of fibres are a disadvantage in separating them from one another by physical methods Their great length causes them to entangle very easily. This effect is greater the greater their length To reduce entanglement to a reasonably small effect the fibres were cut into short lengths When using a liquor to fibre ratio of about 2,000 to 10,000.1 a fibre length of about 0 5 to 2 mm was satisfactory. Even with these short lengths the fibres are about one hundred times as long as they are wide Probably still shorter lengths would be better if there were a convenient method of cutting them The method of preparing the cut lengths of fibres used was to fold a parallel bundle of the fibres in a piece of paper of contrasting colour The paper was folded parallel to the fibres several times. Transverse cuts were made with a sharp pair of scissors sufficiently far across the folded paper to sever the fibres, but not to separate any piece of paper from the main piece After a sufficient number of cuts had been made the paper was unfolded and the short lengths of fibre were shaken on to a suitable surface and collected together

In the early experiments the cut lengths of fibre, after weighing, were placed in a 2 litre beaker containing about 1½ litres of liquor. The fibres were well distributed throughout the liquor by means of vigorous stirring with an electrically driven stirrer in the apparatus. A bent tube was arranged to supply air for the production of the froth required for the flotation

With the simple flotation cell the fibres were floated to the surface by a stream of bubbles emerging from the end of the glass tube just below the stirrer. The stirrer was kept running as the air was driven into the beaker.

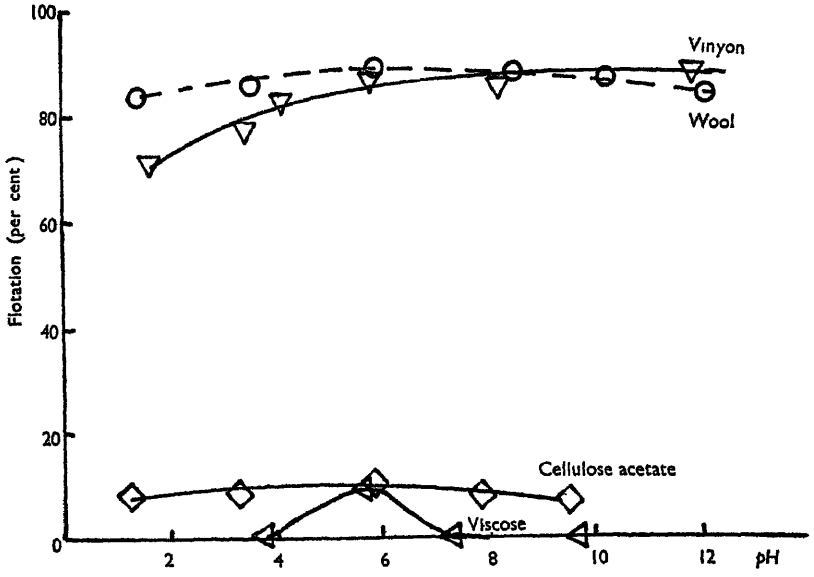

Fig 1

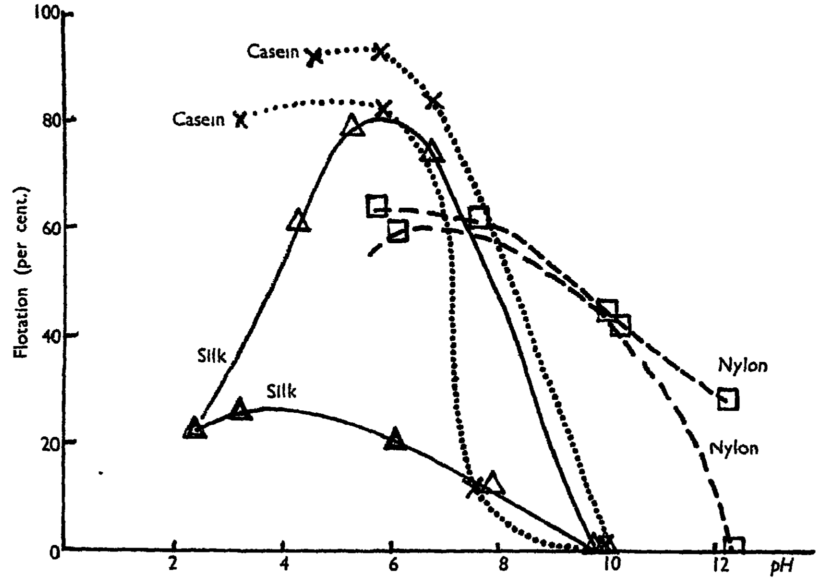

Fig. 2

The upper curve of each pair was obtained by using sodium secondary alkyl sulphate

The motion of the stirrer broke up the bubbles and prevented premature settling of the fibres. After a few minutes the fibres that had floated to the surface were skimmed off with a bent nickel spatula. They were washed off the spatula into a weighed sintered glass filter crucible. All the floated fibres were collected in the crucible and the liquid sucked off. The crucible was then dried and weighed.

To avoid adventitious effects from the presence of soluble finishing agents on the fibres they were given a purification treatment before use. The fibres were boiled in water, except for Vinyon which was treated in water at 60° C , rinsed with further quantities and dried Afterwards they were rinsed with ether and dried again

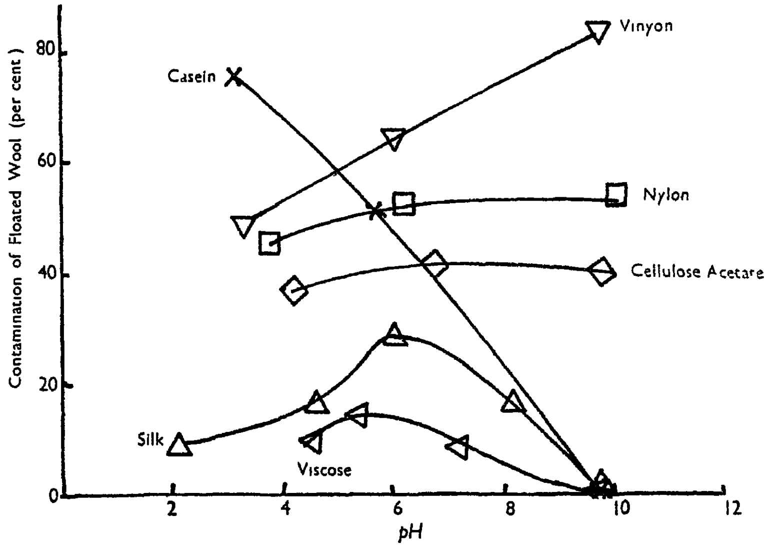

Fig 3

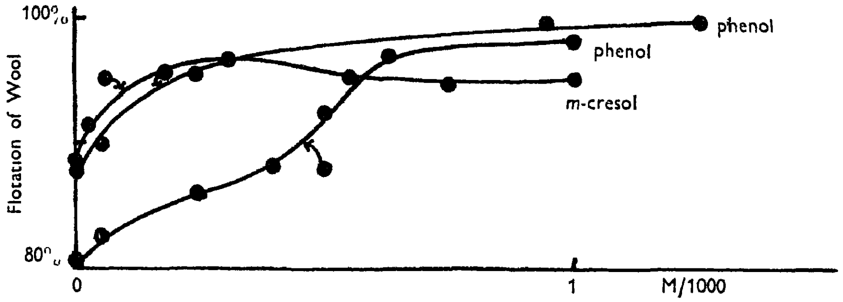

Fig 4

Concentration of phenolic addition in flotation cell.

Flotation experiments were carried out at various *pH* values These were obtained by the use of hydrochloric acid, acetic acid, ammonia and sodium hydroxide. The *pH* value was measured in each case with a glass electrode *pH* meter

Flotation experiments were carried out on wool, Vinyon, cellulose acetate and viscose rayons, casein, silk and nylon fibres taken singly. The recovery by flotation of the fibres at the different *pH* values used is shown in the graphs Figs. 1 and 2 It will be seen that wool and Vinyon fibres, which float most easily, are least dependent on *pH* The flotability of each of the other fibres shows marked dependence on *pH* value The per cent flotation becomes negligible on the alkaline side for casein, silk and nylon fibres It is interesting to note that the flotabilities of viscose and cellulose acetate fibres are very low at all *pH* values examined It had been expected that the flotability of viscose would be low because of its hydrophilic character, but cellulose acetate is appreciably less hydrophilic. Vinyon is notable for being the only fibre tested in which the flotability increased towards the alkaline range.

In the previous experiments no frothing agent was added and consequently it was somewhat difficult to collect the floated fibres from the surface. The effect of adding frothing agents was tested next It was found easier to skim fibres off the surface of the froth than off the liquor itself. The results of experiments with casein silk and nylon fibres with the addition of a commercial secondary alkyl sulphate wetting agent are shown in Fig. 2 Sufficient wetting agent was added to give an approximately 2 millimolar solution in the flotation cell It will be seen that the recovery of silk is considerably improved in the range about *pH* 5-6

Flotation of Fibre Mixtures—Wool and Casein

The results illustrated in Figs 2 and 3 indicated that it should be possible to make a good separation of wool fibres from viscose, casein or silk fibres in the *pH* range from 10 upwards. A mixture of wool and viscose fibres was selected for the first separation experiments. The particular variety of each kind of fibres, the *pH*, the frothing agent and the pre-treatment of the fibres were all varied in turn

Mono-amyl amine, mono-butyl amine and dibutyl amine were each tried at *pH* values in the range 9 2-10 and gave fairly satisfactory separations. The following results, which are the mean of four separate experiments, are typical:

> A mixture of 0 1 gm. each of chrome-dyed wool and direct-dyed viscose staple fibre was placed in the beaker with 1 5 litres of water and 1 c c of 10 per cent mono-amyl amine
>
> The *pH* was adjusted to about 10 with ammonia.
>
> Recovery of fibres· wool, 96 5 per cent , viscose, 97 4 per cent
>
> A microscopical examination of the separated samples showed a slight contamination of about 3-4 per cent in each.

Other surface active agents were tested with the object of depressing the flotability of the viscose without affecting the flotation of the wool. Quantitative measurements were made No improvement was found when using sodium caproate, sodium oleate, saponin, Lissolamine V, or Dispersol V. Cetyl polyglycol ether and Lissapol N were found to be helpful if the mixed fibres were treated with them in 1 per cent solution before placing in the flotation cell. The result of treating a mixture of wool and viscose with 1 per cent. Lissapol N before separating the fibres as described above was found to be a recovery of wool 99 per cent and viscose 100 1 per cent (the figures are the means of two experiments)

The effect of *pH* on the flotation of viscose fibres alone, shown in Fig 2, indicated that the flotation would be a maximum at about *pH* 5-6 and would fall off at higher and lower *pH* values These higher and lower *pH* values should therefore be best for separation from wool An examination was made of the amount of contamination at different *pH* values of the floated wool from wool-viscose mixtures The results are shown in Fig 4 These confirmed the expectations that there would be the worst separation at *pH* 5-6 and better separations at higher and lower values

Experiments with different samples of viscose fibres* showed that there were differences in the ease of separating them from wool As it was known that pre-treatment of regenerated cellulose with dilute alkali increases the swelling in water, viscoses with increasing degrees of swelling were prepared from the same original viscose by treatments with alkali It was found that up to about 6 per cent sodium hydroxide there was a rapid fall in the percentage contamination by viscose of the wool fibres floated to the surface.

---

* Normal and " strong " commercial continuous filament viscose rayon, and staple fibre viscose rayon, and experimental viscose rayons were used

Abrasion of the surface of viscose fibres might also be expected to increase the degree of swelling by disintegrating the skin. Samples of viscose fibres were abraded in various ways and it was found that the contamination of the wool fraction was less for the abraded than for the original viscose fibres

Oven drying at a high temperature might be expected to operate in the opposite direction to an alkaline pre-treatment and to reduce the swelling Samples of viscose fibres which had been oven dried were found to float more readily than the original material and gave more contamination of the wool fraction

A few trials with different dyes did not indicate any marked effect on the flotability of viscose fibres, but chrome-dyed wool appeared to float rather better and to separate from viscose rather better than the undyed fibres. The most striking effect noticed with the different wool samples tested was that the purity of separation was worst for laboratory extracted, degreased raw wool

Rayolanda behaved similarly to viscose and gave a good separation from wool at *pH* 10

Flotation of Fibre Mixtures—Wool and either Casein or Silk

Mixtures of wool with either casein or silk were separated at different *pH* values with the results shown in Fig. 4 In all cases the fibres were given a pre-treatment with 1 per cent Lissapol N as described earlier. It will be seen that a good separation is obtained at *pH* 10.

Flotation of Fibre Mixtures—Wool with Cellulose Acetate or Nylon or Vinyon

Similar separation experiments to those described for casein and silk were carried out with cellulose acetate, nylon and Vinyon with the results shown in Fig 3 It will be seen that at no *pH* tried was there a satisfactory separation. No method was found of improving the separation of Vinyon and wool without modifying the latter, but separations of the other two fibres could be improved by dyeing them with water soluble acetate dyes which had a depressing effect on their flotability.

Chlorination of wool depressed its flotability sufficiently to make it possible to effect a separation from Vinyon It proved practicable to use this device to separate a wool-Vinyon mixture by first chlorinating the mixed fibres After this treatment the Vinyon could be floated away from the chlorinated wool The chlorination was done by treating the fibres with a solution of 3 gm /litre NaOCl (alkaline) for 15 minutes The mixture was then acidified and allowed to stand a further 5 minutes It was then washed, dechlorinated with dilute sodium thiosulphate solution and washed again. Separation was found to be slightly improved if the wet mixed fibres were dried before proceeding with the separation in the usual way

Flotation of Different Kinds of Wool

During the various earlier experiments it had been found that there were marked differences in the flotability of different wool samples.* Various experiments were made to find out the factors which would vary the flotability of wool

As abrasion had reduced the flotability of viscose it was tested with wool and it was found that the greater the degree of abrasion the lower the flotability

In another experiment a lock of wool was taken and the flotabilities of the root and tip ends were examined separately The root ends floated better than the tip ends though the difference was not marked

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* The fibres from dyed and undyed yarns and fabrics together with degreased but otherwise unprocessed wool samples were used

Chlorination by either wet or dry processes was found to produce a profound change in the flotability Chlorinated wool behaved much like casein and could be easily separated from unchlorinated wool at *pH* 10. The effect of chlorine on wool was similar though more marked than the effect of alkali on viscose fibres.

Some substances were tried to improve the flotability of raw wool. It was found that the addition of either phenol or *m*-cresol to the flotation cell considerably improved the flotability The results of three series of experiments with two samples of degreased raw wool are shown in Fig 4.

Flotation of Fibre Mixtures—Casein or Silk and Viscose, Rayolanda or Cotton

The earlier results summarized in Figs 2 and 3 had shown that casein and silk floated fairly well at *pH* 4, whilst at the same *pH* viscose scarcely floated at all Moderately good separations of the protein fibres from the cellulosic ones could be obtained at *pH* 4

Flotation of Fibre Mixtures–Vinyon, Nylon or Cellulose Acetate with other Fibres

Vinyon could be separated fairly nearly completely from all fibres which did not float under alkaline conditions.

Nylon could be partially separated from fibres that did not float under alkaline conditions

Cellulose acetate could be separated partially from viscose, silk and casein.

Velanized cotton floated fairly well under alkaline conditions and could be separated from other fibres which did not float in the alkaline range.

Use of Flotation as an Analytical Method

As the previous experiments had confirmed the presupposition that the flotation method had possibilities as an analytical tool, some test analyses were made using the method The analyses were made on mixtures of known composition and in many cases comparative analyses were made by chemical methods.

The general procedure was as described before The quantities of the materials used were as follows —0·2 gm. mixed fibres which were pretreated with 1 per cent. Lissapol N. The excess liquor was sucked off in a filter crucible and the fibres placed in the flotation cell with 1·5 litres of water plus 25 c c of 1 per cent. phenol plus 0·2 c c of 1 per cent. Teepol X at *pH* 10.

(i) WOOL—VISCOSE UNION FABRIC CROSS-DYED. Composition reputed a 50% 50% mixture

	Wool	Viscose	
Flotation method	43·5%	56·8%	Means of two analyses
Chemical method	44·5%	55·5%	

(ii) WOOL—SILK MIXTURE Composition 30% chrome-dyed wool and 70% undyed wool.

	Wool	Silk
Flotation method	31·2%	68·6%
Chemical method	30·6%	69·4%

(iii) WOOL—CASEIN FELT. Composition reputed 90% wool and 10% casein

	Wool	Casein
Flotation method	87·7%	11·3%

(iv) WOOL—RAYOLANDA MIXTURE Composition 80% chrome-dyed wool and 20% undyed Rayolanda

	Wool	Rayolanda
Flotation method	79·1%	20·0%
Chemical method	79·6%	20·3%

(v) WOOL—CELLULOSE ACETATE MIXTURE Composition 50% chrome-dyed wool and 50% acetate dyed with Cibacet Blue R

	Wool	Acetate
Flotation method	47·7%	53·2%
Chemical method	50·8%	49·2%

(vi) CASEIN—RAYOLANDA MIXTURE. Composition 40% undyed casein and 60% undyed Rayolanda Mixed fibres dyed for 1 min. with 1% Naphthalene Red JS

	Casein	Rayolanda
Flotation method	38 6%	61 2%
Chemical method	40·1%	59·9%

Generally the results indicate that the flotation method gives results of the correct order, but that they are not quite so accurate as the chemical methods where the latter are available The flotation method has the advantage of being quicker and is probably accurate enough for many purposes

Modified Flotation Cell

The removal of floated fibres from the surface of the liquor required some skill and it was considered desirable to have an easier method of separation A cell in which the unfloated fibres could be withdrawn leaving the froth behind was devised The cell of capacity of about 1 litre was provided with a stopcock at the bottom and mounted on the stand of an electric stirrer at a sufficient height to permit a filter flask to be placed underneath The stirrer dips into the cell and just clears a bent tube with its outlet immediately below the centre of the stirrer

In use the cut fibres were placed in the cell, together with about 500 c c. of liquor and thoroughly dispersed with the electric stirrer for about 15 min Air was then bubbled in at the bottom by means of the bent glass tube till a sufficient volume of froth had been produced. The stirrer was now slowed to about 200 r p m to keep the unfloated fibres from settling The liquor with the suspended but unfloated fibres was run out of the flotation cell by cautiously opening the stopcock at the bottom, into a filter crucible immediately below During this operation suction was applied to the filter crucible This removed the liquor leaving the fibres in the crucible The tap was turned off before any of the froth escaped The liquor was now returned to the cell and the cycle of operations repeated By this means most of the unfloated fibres were drawn off into the crucible The first crucible was now replaced by another one and the froth broken by amyl alcohol and ethyl alcohol and these fibres also were drawn off into the crucible below The crucibles and fibres were dried and weighed

Trial Analyses with New Cell

Several trial analyses were made using the new flotation cell Fibres (0 1-0 2 gm) were transferred to a sintered glass crucible and treated with 1 per cent Lissapol N, excess of which was sucked off They were then transferred to the cell which contained 600 c c water plus 1 c c concentrated ammonia plus 10 c c 1 per cent. phenol The fibres were thoroughly dispersed with the electric stirrer and then treated as described above The results of typical analyses were

(i) WOOL—CASEIN MIXTURE

	Wool	Casein
Taken	0 100 gm	0 084 gm.
Flotation method	0 106 gm	0 081 gm

The slight total gain in weight of fibres is probably due to differences in condition

(ii) WOOL—CHLORINATED WOOL (Wet process in the laboratory)

	Wool	Chlorinated Wool
Taken .	0 100 gm	0 100 gm
Flotation method	0 110 gm	0 090 gm.

(iii) VINYON—CHLORINATED WOOL (Wet process in the laboratory)

	Vinyon	Chlorinated Wool
Taken	0 100 gm	0 100 gm
Flotation method	0 090 gm	0 109 gm

Conclusions and Discussion

Hydrophobic fibres such as wool and Vinyon float well whereas hydrophilic fibres such as viscose and cotton have only a slight tendency to float. The absence of hydrophilic groups in Vinyon appears a sufficient explanation of its good flotability With wool it is possible that the structure of the fibre surface has a favourable effect on the tendency of air bubbles to stick to the fibres

It was observed that any treatment which favoured making the fibres more hydrophobic like Velanizing cotton or high temperature drying of viscose favoured flotation. Treatments which made fibres more hydrophilic like an alkaline treatment of viscose or chlorinating wool depressed the tendency to float

Treatment with some amphipathic substances changed the tendency to float of some fibres. Phenol and cresol showed a selective effect in appreciably increasing the tendency of wool fibres to float out of several fibre mixtures. Non-ionic wetting agents depressed the flotation tendency of all fibres Anionic wetting agents form insoluble complexes with water soluble protein.[12] It was therefore not unexpected to find that sodium secondary alkyl sulphate increased the hydrophobic character and flotability of silk and casein

Dyes are known to be selective flotation agents for mineral particles [13] Many dyes are amphipathic substances which are selectively absorbed by different fibres The nature of the effect of dyes on the flotation tendency of fibres depends on whether the absorbed dye is attached to the fibre by its hydrophilic or hydrophobic groups. If the former, then the fibre should become more hydrophobic whereas if it is the latter, then the fibre should become more hydrophilic There was not sufficient time available to explore this subject thoroughly but there were indications that dyeing the protein fibres and nylon with the water soluble dyes of the acid or basic types increased the flotability Dyeing cellulose acetate and nylon with the water soluble acetate colours decreased their flotability

pH had a considerable effect on the flotation of most fibres with the exceptions of wool and Vinyon which floated well throughout the range tested and viscose which scarcely floated in the same range The general shapes of the flotation—*pH* curves were similar to those which have been reported in the literature for mineral particles [14] A comparison of the flotation—*pH* curves of fibres with the corresponding electrokinetic potentials[15] showed no correlation This agrees with the statements of Wark[2] and Adam[5] for mineral particles

REFERENCES

[1] Edser " Flotation " in Fourth Report on Colloid Chemistry *D S I R*, 1922
[2] Wark. " Principles of Flotation," Melbourne, 1942
[3] Schulman *J. Phys. Chem*, 1942, 46, 886
[4] Sunderland *Ibid*, 1948, 52, 394
[5] Adam. " Physics and Chemistry of Surfaces," Oxford, 3rd Edition, 1941
[6] Clanton, Cameron and Magoffin *Text Research,* 1939, 10, 201
[7] Suprenant, Magoffin and Cameron *Ibid*, 1940, 11, 726
[8] Howlett, Morley and Urquhart *J Text Inst*, 1942, 33, T75.
[9] Carter and Consden *J. Text Inst*, 1946, 37, T227
[10] Larose *Can J Research,* 1938, B16, 61
[11] Skinkle, " Textile Testing " Howes Publishing Co, New York, 1940
[12] Pankhurst and Smith *Trans Faraday Soc*, 1944, 40, 565
[13] Zapadanski *Tsvetnye Met*, 1947, 20, 28, *Chem Abs*, 1948, 22, 4005.
[14] Talmud and Lubman *Koll Z*, 1930, 50, 159, 163
[15] Neale and Peters *Trans Faraday Soc*, 1946, 42, 478

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24—THE EFFECT OF TEMPERATURE IN THE SCOURING OF MERINO WOOL ON SUBSEQUENT PROCESSES

By P. P. TOWNEND and W. TWEEDIE

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When wool is to be spun it must first be scoured to remove the impurities which adhere to it, *viz*, wool wax, suint and earthy matter. These are removed by passing the wool through a series of wash bowls containing solutions of soap and sodium carbonate heated to certain temperatures. For merino wool, the temperatures of the liquors in succeeding bowls usually range from 125° F in the first, to 100° F in the fourth or final bowl The object of the present paper is to demonstrate how the temperature of the scouring liquors affects the behaviour of the wool during its conversion into worsted yarn.

EXPERIMENTAL. FIRST SERIES.

Scouring

Three 15 lb lots of 64s greasy Australian matchings were drawn from the same blend and labelled A1, B1 and C1 These were taken to a scouring machine which consists of two bowls, each having a capacity of 300 gallons Squeeze rollers are placed at the end of each bowl so that the wool passes from the one to the other automatically Propulsion in each bowl is by the swing harrow system. The object was to subject each lot to a four bowl scour using a different temperature range in each case but the same concentration of scouring agent. In order to achieve this it was necessary to pass each batch twice through the two-bowl machine Throughout each test the concentration of the scouring liquor remained the same in each individual bowl for all three lots of wool These data are given in the following table.

	Concentration of	
	Soap	Sodium Carbonate
Bowl 1	0 14%	0 06%
Bowl 2	0 14%	0 06%
Bowl 3	0 07%	0 03%
Bowl 4	—	—

The temperatures of the bowls were, however, varied as follows.

	Temperature for		
	Lot A1	Lot B1	Lot C1
Bowl 1	125° F	150° F	180° F
Bowl 2	120° F	144° F	173° F
Bowl 3	115° F	138° F	166° F
Bowl 4	110° F	132° F	159° F

During scouring the following procedure was adopted The two bowls were filled with water to their capacity and the necessary amounts of soap and sodium carbonate added to the side settling tank By means of a steam injector the contents of bowls one and two were raised to 125° F and 120° F, respectively, at the same time the scouring agents were allowed to circulate through their respective bowls by the normal pump system When these temperatures were reached lot A1 was fed to the machine and passed through the two bowls After delivery by the squeeze rollers of the second bowl A1 was collected and stored in a can.

Immediately after lot A1 had passed through the machine more steam was injected into the water in the bowls and the temperatures raised to 150° F. and 144° F. Lot B1 was then passed through the machine in a similar manner to A1; being collected as it emerged from the squeeze rollers of the second bowl.

After lot B1 had passed through the machine more steam was injected and the temperature of the liquors were raised to 180° F and 173° F. Lot C1 was then passed through the machine and collected as before.

Immediately after lot C1 had passed through the machine both bowls were emptied and clean water was run in. Further scouring reagents were then added to bring the solutions up to the required concentrations for the third and fourth bowls of the scouring set, the last bowl in this case being left as a clean water rinse.

When the agents had been added, the solutions in the bowls were raised to the required temperatures for the third and fourth bowl scours of lot A1. Lot A1 was then removed from the can, in which it had been stored, and passed through the machine as before. After emerging from the machine the wool was collected and replaced in the can.

The water in the bowls was then raised to the required temperatures for the third and fourth bowls of lot B1, which was passed through as before. Finally the water was raised to the temperatures required for lot C1 which was likewise passed through and collected in a can.

All the scouring operations formed an unbroken sequence, the whole procedure taking place in the same morning.

During scouring, samples of the liquors from the various bowls were collected in small specimen bottles and subsequently tested for *pH* value. This procedure was intended to act as a check on the strengths of the different solutions. The results are given in the following table.

	pH Lot A1	*pH* Lot B1	*pH* Lot C1
Bowl 1	10·27	10·27	10·06
Bowl 2	10·38	10·38	10·37
Bowl 3	10·43	10·41	10·41
Bowl 4	9·29	9·65	9·66

These figures illustrate that all three lots of wool were, so far as *pH* is concerned, scoured under similar conditions.

Samples of wool were also taken as each lot emerged from the various bowls. Ether and alcohol extractions were made on these samples using the Soxhlet apparatus. These serve to demonstrate the amounts of impurity remaining on the different batches of wool and it will be seen that each was scoured down to a commercial level.

Details are given in the following table:

	Lot A1		Lot B1		Lot C1	
	% Ether Extract	% Alcohol Extract	% Ether Extract	% Alcohol Extract	% Ether Extract	% Alcohol Extract
Bowl 1	2·05	1·16	1·68	0·94	2·15	1·22
Bowl 2	0·73	0·20	0·41	1·00	0·49	1·32
Bowl 3	0·54	0·86	0·43	1·01	0·42	1·20
Bowl 4	0·39	0·77	0·33	0·93	0·35	1·19

Carding

After lot C1 had passed through the last bowl all three lots were taken, in the cans in which they had been collected, to the botany worsted card. No drying operation was performed, the wool being carded at the moisture content at which it left the squeeze rollers of the last bowl of the scouring set.

Lot A1 of the scoured wool was then placed in the hopper of the card, which in turn fed the wool to the carding machine. This is a 30 inch wide card having two swifts and four lickers The clothing on the swifts is 120, 10, 32 and 140, 12, 34, respectively, swift speeds being 118 r.p m

The wool was delivered from this machine in the form of balls In all, approximately 8 lb of wool was carded from lot A1.

When the last lot of wool from lot A1 had been delivered by the hopper the machine was allowed partially to run off Lot B1 was then placed into the hopper. When the sliver emerging from the card became thick it was then considered that lot B1 was passing through the card, and that lot A1 had run off completely Lot B1 was then collected.

When the hopper was emptied of lot B1 it was followed by lot C1 in the same manner that B1 had followed A1

Since the wool was carded in the damp state, samples of each lot were taken from the feed sheet of the card at regular intervals and placed in air tight containers. This wool was subsequently tested for moisture content by drying in a conditioning oven. The following figures were obtained.

	Lot A1	Lot B1	Lot C1
Regain . .	53 5%	53 9%	52 0%

It will be seen that all three lots were carded at approximately the same moisture content.

Gilling and Combing

The slivers were delivered from the card weighing 336 drams per forty yards After carding lot A1 was gilled with six ends up and a draft of three on a strong box having 12 pins per inch. As the wool emerged from the strong box it was subjected to a conditioning action. The object of this gilling operation was to effect a mixing and parallelising of the fibres

Lots B1 and C1 followed in turn and were each subjected to the same treatment.

All three lots were then passed twice through an intersecting gill box The fallers of this machine had 18 pins per inch and the wool was gilled with four ends up and a draft of approximately six This treatment gave a sliver weight of 40 drams per 5 yards desired for the combing operation

Twelve slivers of lot A1 were then fed to the French comb The top sliver was collected in a can and the noil deposited in the noil bin When lot A1 had been combed the top and noil were both collected and weighed, so that the tearage in combing could be calculated The same procedure was adopted for lots B1 and C1 The figures for tear are given below·

Lot	Tear
A1	15 2 1
B1	13 3 1
C1	10 6 1

Lots A1, B1 and C1 were then passed through a finisher gill box three times with four ends up and a draft of four giving a top weighing 256 drams per 40 yards. The pinning of the fallers on the finishing gill box was 18 pins per inch

Drawing and Spinning

The three tops made from lots A1, B1 and C1 were then drawn and spun. A short drawing process was purposely chosen to emphasise any irregularities and weaknesses due to the different treatments in scouring. The scheme of drawing is set out in the following table:

Machine	Doublings	Draft	Wt /40 yds
Spindle gill	4	6·4	160 drams
First finisher	1	4·7	34 ,,
Second finisher	2	5·0	13·6 ,,
Reducer	2	5·0	5·5 ,,
Rover	2	5·0	2·2 ,,

The three lots of rovings were then cap spun to 40s worsted count and 14 turns per inch The draft employed during spinning was 4·7 and the spindles of the frame revolved at 6,000 r.p.m.

Tests were then carried out on the various slivers and yarns These will be discussed in the next section. Before going on to this section, however, it will be more convenient if the subsequent experimental work is described at this stage

Experimental work is always difficult with such a variable material as raw wool One can never be sure that the effect of any variable, such as the temperature in scouring, can be clearly shown by one series of experiments, for there are so many other processing variables which might also affect the materials and mask the effect of that particular one under consideration. For this reason then, the whole experimental work was repeated on a second batch of wool drawn from the same source as the first

EXPERIMENTAL. SECOND SERIES.

Scouring

The experiment was repeated in precisely the same manner as before with three further 15 lb lots of similar wool, this time labelled lots A2, B2 and C2 Once again samples were taken of the various liquors during scouring, which were subsequently tested for *pH* value The results were as given below.

	pH Lot A2	*pH* Lot B2	*pH* Lot C2
Bowl 1	10·16	10·07	9·95
Bowl 2	10·09	10·06	10·00
Bowl 3	10·20	10·28	10·21
Bowl 4	7·69	8·40	8·51

These figures indicate that all three lots of wool were again treated at approximately the same *pH* in the various bowls

Samples of the wool were again taken from each bowl during scouring and were extracted, as in the previous experiment, with ether and alcohol in the Soxhlet apparatus. The results of the tests are given in the following table

	Lot A2		Lot B2		Lot C2	
	% Ether extract	% Alcohol extract	% Ether extract	% Alcohol extract	% Ether extract	% Alcohol extract
Bowl 1 .	2 61	1 70	1 86	1 40	3 10	1 15
Bowl 2	1 06	2 10	0 41	2 05	0 38	1 66
Bowl 3 .	0·41	0 93	0 44	—	0 42	—
Bowl 4 ..	0 54	—	0 40	—	0 45	—

Carding

After the last lot had been scoured the wool was transported to the worsted card as before and once again carded in the wet state, immediately after scouring. The routine followed during carding was precisely the same as in the first experiment

Samples of each lot were taken from the feed sheet at regular intervals during the carding operation and subsequently tested for moisture content by drying in a conditioning oven The results of the tests are given in the following table

	Lot A2	Lot B2	Lot C2
Regain .	31%	28%	26 6%

Gilling and Combing

After carding the three lots of wool were then processed as in experiment one, with the same doublings and drafts as before They were then combed in turn on the French comb, giving the following tears·

Lots A2, B2 and C2 were then finished into the form of a top as in experiment one

Lot	Tear
A2	12 2 1
B2	10 8 1
C2	8 2 1

Drawing and Spinning

The three tops were again taken to the open drawing machinery and reduced to roving form in the same manner as in experiment one, using the same drafts and doublings

The rovings were then spun to 40s count with 14 turns per inch in the same manner as lots A1, B1 and C1.

TESTING PROCEDURE

Carded Slivers

It was hoped that two facts might be established from the carded slivers, *viz.*, the extent of fibre breakage and the degree of nep formation in carding which might be attributed to the different temperatures used in scouring

To carry out these tests, nine two foot sample lengths of sliver were chosen at random from each of the three card balls

From lot A1 nine tufts of approximately 250 fibres each were drawn using the Townend Tong Method[1]—one tuft from each two foot length—and measured by forceps to the nearest centimetre From these figures the mean fibre length and the standard deviation of each tuft was calculated This test was repeated for lots B1, C1, A2, B2 and C2 The results of these measurements are given in Tables I and II, whilst the fibre length distributions are shown in Figs 1 and 2

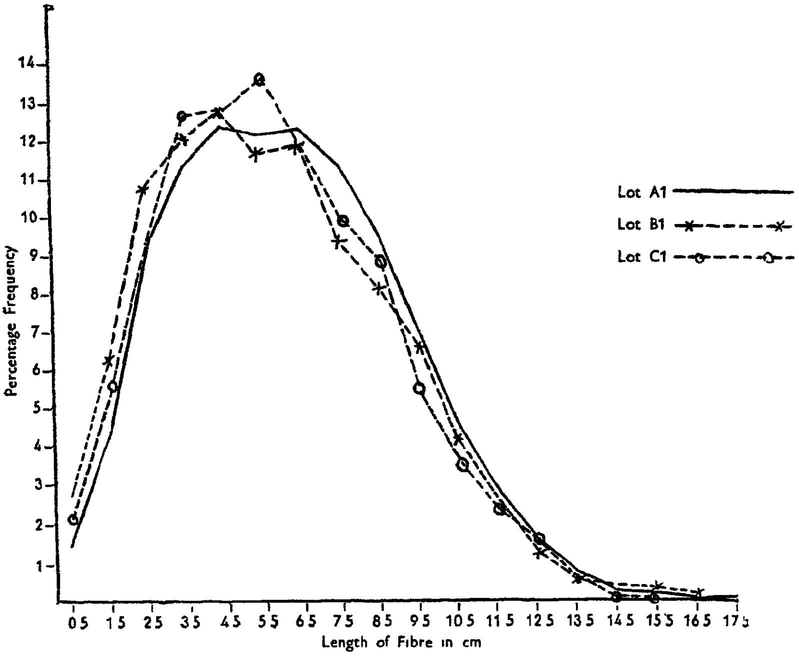
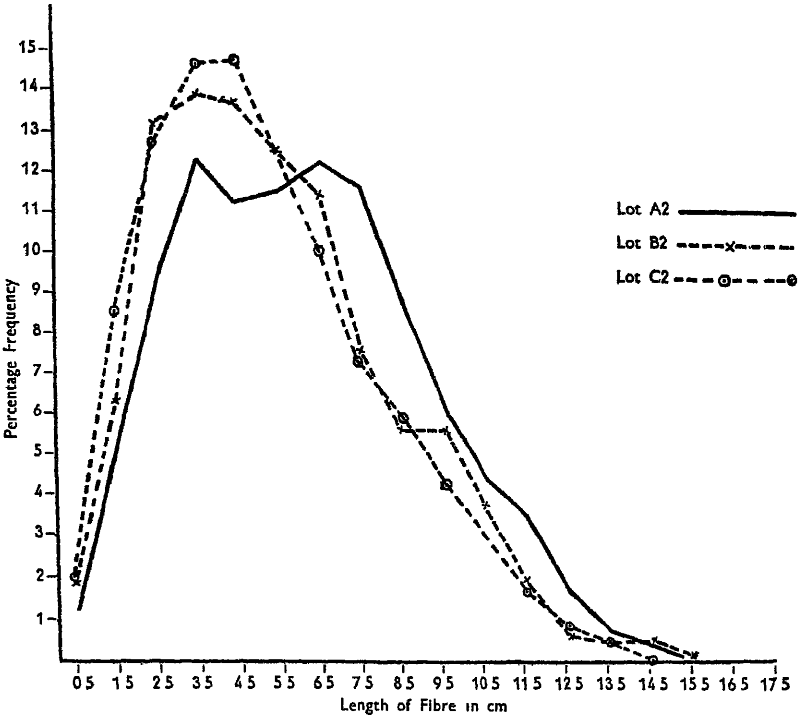

Percentage Frequency
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0 5
1 5
2 5
3 5
4 5
5 5
6 5
7 5
8 5
9 5
10 5
11 5
12 5
13 5
14 5
15 5
16 5
17 5
Length of Fibre in cm
Lot A1
Lot B1
Lot C1

Fig 1


Percentage Frequency
15
14
13
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11
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1 5
2 5
3 5
4 5
5 5
6 5
7 5
8 5
9 5
10 5
11 5
12 5
13 5
14 5
15 5
16 5
17 5
Length of Fibre in cm
Lot A2
Lot B2
Lot C2

Fig 2

The two foot lengths were then, in every case, cut into halves and from lot A1 nine one foot lengths were taken and examined for nep content When the neps had been counted the nine one foot lengths were put into separate packages and conditioned for 48 hours at 65° F. and 70 per cent R.H.—the object of conditioning being that all results would be comparable by weight, being at the same humidity Each foot length was then weighed in turn and the number of neps per gram of sliver calculated

A similar procedure was adopted for lots B1, C1, A2, B2 and C2

It was subsequently found necessary to repeat the nep counts on the second halves of the slivers belonging to lots A1, B1 and C1 since a difference arose between the results for the two series The figures for neppiness are given in Tables I and II

Top Examination

Representative samples were selected from each of the different lots of tops and a further fibre length determination was made, again using the Townend Tong Method. Three tufts of approximately 250 fibres each were measured in each case The fibre diagrams are given in Figs 3 and 4, whilst the mean fibre lengths are shown in Tables I and II

Testing of Yarns

From each lot twelve full bobbins of yarn were spun to 40s worsted count with 14 turns per inch These were conditioned for 24 hours at 65° F. and 70 per cent R H, after which they were tested for strength From each bobbin, two 300 yard hanks were wound on a 54-inch reel and tested for strength on a Goodbrand's testing machine Since there were twelve bobbins in each lot, the average strength of each yarn was obtained as a mean of 24 tests. These figures are given in Tables I and II

Table I

First Series

	Lot A1	Lot B1	Lot C1
Mean fibre length of card sliver, cm	6·2	5·8	5·8
Standard deviation, cm	2·9	2·9	2·8
Mean neps per gram in card sliver	5·6 3·4	4·2 3·3	4·9 3·8
Tear in combing	15·2 : 1	13·3 : 1	10·6 : 1
Mean fibre length of top, cm	7·5	7·0	6·5
Standard deviation, cm	2·9	2·9	2·8
Mean breaking load of yarn (1/40s worsted 14 t p i) lb	69·3	61·1	58·2

Table II

Second Series

	Lot A2	Lot B2	Lot C2
Mean fibre length of card sliver, cm	6·2	5·5	5·2
Standard deviation, cm	3·0	2·9	2·9
Mean neps per gram in card sliver	4·5	6·6	8·0
Tear in combing	12·2 : 1	10·8 : 1	8·2 : 1
Mean fibre length of top, cm	7·5	7·0	6·8
Standard deviation, cm	3·0	3·1	3·0
Mean breaking load of yarn (1/40s worsted 14 t p i) lb	69·7	71·1	64·1

quoted for neps per gram of sliver are so small, one cannot draw any conclusion from them.

A consideration of the results obtained in the second series confirms the conclusions drawn from the first series Fibre breakage in carding, the tear in combing and the mean fibre length of the tops all agree with the findings of series 1 There is a difference between the figures as a whole, for tear, in that series 2 gave slightly smaller tears, but the order is the same

Two differences exist between the two series, in that the *pH* values of the last bowl of the second series were more in line with industrial practice than the first series, and secondly, the moisture content of the wool going to the card was considerably lower, but these differences do not appear to have influenced the particular tests made on the lots of wool

SUMMARY

Three batches of 64s Australian wool were washed by a four bowl scour using the same concentration of scouring agent, but with different ranges of temperature These varied between 125°–110° F, 150°–130° F and 180°–159° F for the three wools

Tests were made for fibre breakage and nep formation during carding, tear in combing, fibre diagram of the three tops and yarn strength after spinning. These revealed that the wool scoured at the lower temperature range suffered considerably less breakage in carding, gave a better tear in combing and a greater mean fibre length in the top There was no significant difference in neppiness of card web between the three lots.

A second series of experiments confirmed these findings

As regards yarn strength the results of the two series were conflicting and it was not possible to relate temperature in scouring to this property of the yarn

ACKNOWLEDGEMENT

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REFERENCE

[1] Townend, S *J Text Inst*, 1938, **29**, T57

Department of Textile Industries,
University of Leeds.

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25—RAPID METHODS FOR DETERMINING THE CUPRAMMONIUM FLUIDITY OF COTTON CELLULOSE

By F. Howlett and (the late) D. Belward

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INTRODUCTION AND SUMMARY

Largely by reason of the pioneer work of the British Cotton Industry Research Association[1,2] the cuprammonium fluidity of cotton is currently regarded as a valuable index of chemical degradation. For special purposes, however, improvements to the method are needed At present a determination takes about twenty hours to complete, and although Clibbens and Geake[1] record fluidity data obtained after shaking the solution for two hours, this does not seem to have been pursued Without doubt the control of many chemical processes for treating cellulose would benefit by a rapid method which retained the accuracy of standard practice. A satisfactory modification for viscose rayon has already been suggested by Ridge and Bowden [3] They show that the rayon can be dissolved rapidly, and serious oxidative degradation avoided, by shaking with cuprammonium without precautions to eliminate air. The solution is then transferred to the viscometer and the whole process completed in about half an hour Recently the same method has again been proposed,[4] this time for degraded celluloses of chain-length below 1,000 glucose units Admission of air to cuprammonium solutions of cotton itself was, however, found to be detrimental It appears feasible to assume that given some means of preventing this degradation the dissolution of the cotton could be accomplished rapidly. Such a means has already been provided by W. A S. White and T N Richardson[5] who found that the degradation occurring when cuprammonium solutions of linen are filtered could best be prevented by the addition of pyrogallol They do in fact suggest that the reagent might prove valuable in special applications of the fluidity method to cotton It has been successfully used here for a method in which the cotton is dissolved by hand-shaking for ten minutes in an incompletely-filled bottle. Though the method is applicable to air-dry cotton the main emphasis here is on wet cotton when the above dissolution technique is preceded by a drying process in which the sample is first washed with acetone and then dried in a hot air stream for two minutes. The whole operation (termed Method I) occupies rather under half an hour.

The other method of approach to this problem is to dissolve the damp cotton in cuprammonium, to determine the moisture content separately, and to use some relation between concentration and viscosity for conversion of the results to ½ per cent. concentration. Though some 2½ hours are required to obtain a result this method has advantages in that normal oven-drying is used, and that the filtration essential in Method I is eliminated The recalculation of a result obtained at some arbitrary concentration to that at ½ per cent. concentration is facilitated by a nomogram. This latter device is of course valuable in normal fluidity work when, say, insufficient material is available J. R. Womersley[6] has previously designed a nomogram based on the Farrow and Neale equation.[7] This equation, however, has two constants which can alter with the cotton[8] and Womersley's nomogram is restricted to the conversion of results from 2 per cent. to ½ per cent concentration, which is nowadays seldom, if ever, required.

The methods described here are merely extensions of the established B.C I.R.A technique, and the latter was used for checking the results obtained. It is stressed that only loose cotton has been considered, although there is no reason to doubt the application to normally-finished fabrics.

EXPERIMENTAL

The viscometers and cuprammonium solvent are those recommended by the British Cotton Industry Research Association,[1,2] whose experimental procedure is also followed for the most part except for the modifications described here These shorten the time required to obtain a fluidity result

It is assumed that representative sampling is adhered to and that the cotton is hand-opened.

Method 1 : Experimental Instructions

The principle used is first to dry the cotton and then to prepare from it a solution of exactly ½ per cent. concentration using a degradation inhibitor

(i) Remove the water from about 1 g. damp cotton by washing with three changes of acetone.

(ii) Remove excess acetone by squeezing and dry for two minutes in a current of air at about 100° C

(iii) Weigh about 0·2 g. of the dry cotton into a 2 oz glass-stoppered bottle and add to it, from a burette or measuring cylinder, enough cuprammonium to give a ½ per cent solution (0·5 g dry cotton in 100 c c solvent) Alternatively weigh exactly 0 25 g cotton quickly and add 50 c c cuprammonium Finally add from a dropping bottle six drops (about 0·3 c c) of a solution containing 50 g. pyrogallol in 100 c c water.

(iv) Shake the bottle vigorously for ten minutes.

(v) Filter the solution into the viscometer through a fritted glass pressure filter of porosity No. 2, and determine the fluidity at 20° C

The following explanatory comments on these instructions include details of satisfactorily established techniques.

Two types of hot-air blower have been used for the drying One was a commercial hair-drier, the other, with which all recorded results were obtained, was a more robust apparatus mounted on a base-board and made by Messrs Reynolds and Branson Ltd The cotton was contained loosely in a small cylinder of copper gauze which fitted over the air jet from which issued 20 cu ft /per minute Where compressed air is available a simple alternative is to pass a slow stream over an electric heater element or through a gas-heated metal tube. A preliminary test of the drying efficiency of any apparatus is always desirable.

The procedure of weighing exactly 0 25 g dry cotton, though theoretically unsound on account of absorption of water by the cotton, has nevertheless given accurate results

Attempts to replace hand-shaking by high speed stirring were not successful since swollen cellulose particles adhered to the sides of the vessel above the liquid level. It is possible, however, to employ a rapidly reciprocating shaker provided that the bottles or phials are almost full and are lying on their sides Even with hand-shaking it is desirable to have the bottle well over half-full and in this connection 2 oz bottles were found suitable and have been used in this work

A hand bellows can be used for the filtration under pressure or alternatively suction is possible though less satisfactory Filtration is desirable to remove undissolved particles that are occasionally present and which, though insignificantly affecting the concentration, might cause blockage of the viscometer capillary

By omitting the drying step and making the usual allowance of 6 per cent. contained moisture the method can be used for air-dry cottons

Method 1 : Experimental Development and Results

A preliminary investigation showed that two drops (about 0 1 c c) of the pyrogallol solution was the minimum required to prevent degradation under the conditions used The considerable excess of six drops chosen for routine use had little effect on the fluidity of the solvent (reducing it from 72 to 71 reciprocal poises) or on the fluidity of a cotton solution (reducing it from 5 4 to 5 2 reciprocal poises). This addition of pyrogallol was found to be completely effective in preventing degradation of the cellulose when the dissolution technique described above was used Furthermore it was found for cottons of fluidity ranging from 3 to 16 units, that it was not necessary to shield the solutions from the light during their preparation and thus white glass bottles are permissible for this purpose In this connection it is of interest that the solutions themselves become black on addition of the pyrogallol

No increase in fluidity occurred on leaving the solution to stand in daylight for some hours provided the bottles remained stoppered. Even after standing for 24 hours the fluidity of a solution increased only from 5 2 to 5 8

In tests of the application of the method to damp cottons white bottles were used and results for cottons of different fluidity are given in Table I From the comparison with controls it is concluded that the method is adequate for industrial use

Table I

Fluidity	
Method 1	B C I R A control
4 0, 4 0	3 1
4 2, 4 3	3 8
4 3, 4 7	4 1
5 2, 5 4	5 2
5 6, 6 1	5 2
6 7, 7 0	6 7
11 3, —	12 2
16 0, —	15·8

The action of the pyrogallol is probably twofold Some of the oxygen present will be absorbed directly, but in addition pyrogallol rapidly reduces the copper in cuprammonium to the cuprous state which would then itself remove oxygen In this there is a similarity to a rapid fluidity method proposed by H Doering[9] in which metallic copper was added to the cuprammonium before dissolution of the cellulose.

Method 2 : Experimental Instructions

The principle used here is to dissolve a known weight of damp cotton in cuprammonium, to determine its moisture content separately, and to use a relation between concentration and fluidity for conversion of the result to exactly ½ per cent concentration This is not so rapid as Method 1, but the relation between concentration and viscosity is itself useful in standard fluidity practice where inadequate amounts of material are available

(i) Determine the moisture content by drying about 1 g. of the damp cotton for 2 hours at 110° C.

(ii) Weigh accurately about 0·1 g damp cotton, transfer to the viscometer, and dissolve in cuprammonium for two hours Determine the fluidity at 20° C

(iii) Calculate the dry weight of cotton used and express this as grams of dry cotton per 100 c c of solvent (from the known volume of the viscometer). Convert the fluidity to that at ½ per cent concentration using the nomogram

The following additional notes to these instructions are necessary

For the drying, which takes place in an oven, it is desirable to use hand-opened cotton in a wide shallow weighing bottle

The speed of rotation of the wheel recommended by the British Cotton Industry Research Association for dissolving the cotton should be increased to about twelve revolutions per minute, which is treble the normal rate

For stirring purposes the usual amount (0 7 c c) of mercury is added to the viscometer.

To use the nomogram the experimental fluidity is marked on scale A and the experimental concentration on scale C The line joining these two points then cuts the fluidity scale B at the required value for ½ per cent concentration It is advantageous to use a piece of thread or wire or alternatively a linear mark on a colourless ruler instead of drawing on the nomogram itself

Method 2 : Experimental Development and Results

The basis of this method is that there is a relation between fluidity and concentration of cellulose solutions which holds sufficiently for most fluidity work It has been previously demonstrated[10] that the following equation is valid for cuprammonium solution of rayons

$$\eta_r^{1/n} - 1 = p\ c$$

where η_r is the viscosity of the solution relative to that of the solvent,

n has any value between 6 and 10,

p is a constant for each sample of cellulose,

c is the concentration of cellulose in solution

That this equation also holds approximately for solutions of cotton cellulose is shown in Table II Here three different samples of cotton are considered and the value of $(\eta_r^{1/n} - 1)/c$ should remain constant with concentration for each value of n

The value of n was taken as 6 and the equation, when rearranged therefore becomes

$$(f_0/f)^{1/6} - 1 = p\ c$$

where f_0 is the fluidity of the solvent, taken as 70 reciprocal poises and f is the fluidity of the solution

The nomogram (Fig 1) based on this relation was constructed to apply to cottons of fluidity from 3 to 40 in ½ per cent solution, details of its construction are given in the Appendix. Its validity was initially tested with the results from sample 2 (Table II) by converting these to ½ per cent. concentration The several values found should, of course, be identical, and also should approximate to the observed normal fluidity Table III shows that this is reasonably true

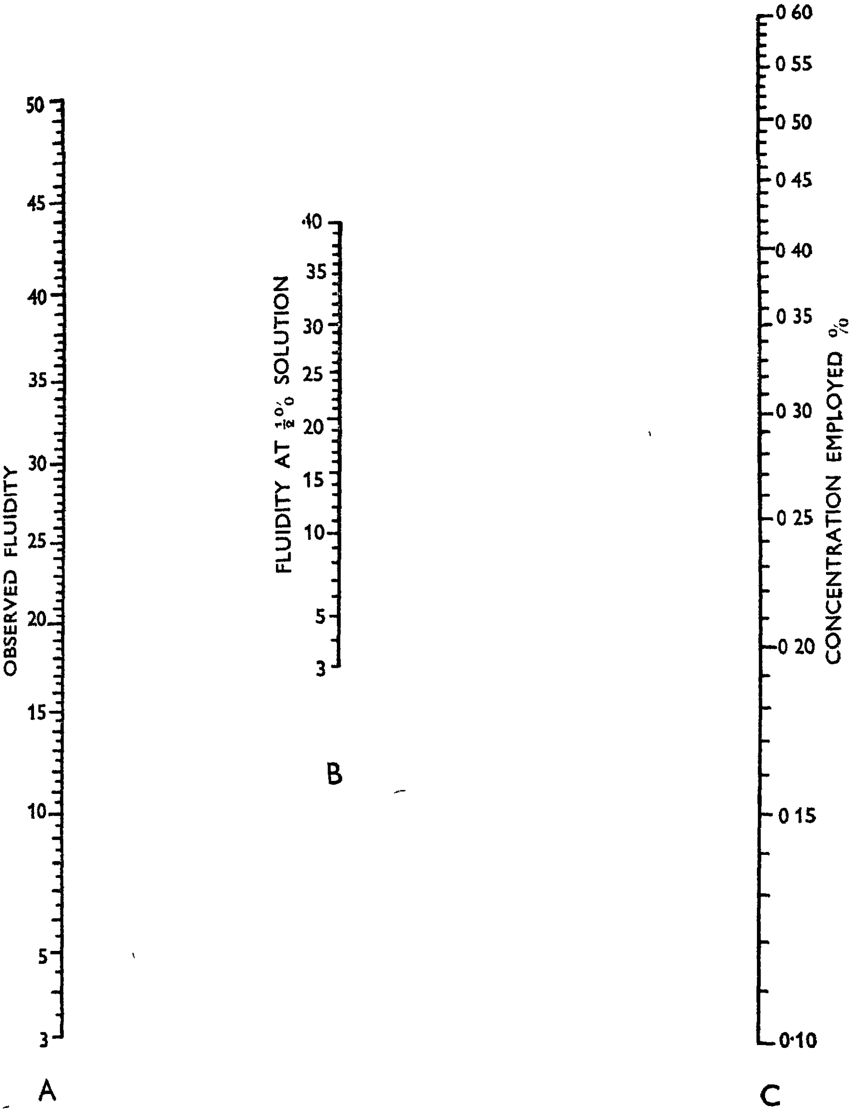

Fig 1
Nomogram for the conversion of fluidities to a basis of ½% from determinations made at other concentrations

The nomogram was further tested with seven cottons whose fluidities covered a wide range Their fluidities were found at exactly ¼ per cent. concentration by overnight dissolution and the results then converted to ½ per cent concentration These values are compared in Table IV with experimental results obtained at exactly ½ per cent concentration

Table II

Cotton sample	Concentration of solution %	Viscosity of solution *cp*	$(\eta_r^{1/n} - 1)/c$		
			$n=4$	$n=6$	$n=8$
1	0·467	17·88	1·9	1·1	0·8
	0·339	10·29	1·9	1·1	0·8
	0·281	9·04	2·1	1·2	0·9
	0·188	4·84	2·0	1·2	0·9
	0·084	2·45	1·7	1·1	0·8
2	0·526	19·42	1·8	1·0	0·7
	0·486	18·68	1·9	1·1	0·8
	0·470	15·97	1·8	1·1	0·8
	0·390	10·49	1·7	1·0	0·7
	0·238	5·52	1·7	1·1	0·8
	0·102	2·73	1·8	1·2	0·9
3	0·743	19·42	1·2	0·7	0·5
	0·518	12·39	1·4	0·8	0·6
	0·494	10·91	1·3	0·8	0·5
	0·397	7·91	1·3	0·8	0·7
	0·280	5·23	1·3	0·8	0·6

Table III

Concentration of solution %	Observed fluidity	Recalculated fluidity
0·526	5·2	5·3
0·486	5·9	5·0
0·470	6·3	5·0
0·390	9·5	5·8
0·238	18·1	5·0
0·102	36·6	4·7

Observed fluidity at ½ per cent concentration was 5·1

Table IV

Fluidity in ¼% solution	Fluidity in ½% solution	
	Calculated	Observed
14·3	3·9	5·2
14·6	4·2	5·5
18·7	6·2	6·7
21·6	8·0	8·4
31·0	14·9	14·8
35·8	19·4	18·3
37·1	20·7	20·3

The foregoing results all refer to air-dry cotton

An estimate of the time required for drying was made with three portions of the same sample of damp cotton heated in an ordinary laboratory oven at 110° C. Each sample was weighed at intervals and Table V shows clearly that the two hours suggested is adequate for samples containing up to 50 per cent. of water

Table V

Time of drying (hours)	Calculated moisture content %		
	Sample 1	Sample 2	Sample 3
1½	45·9	45·3	46·1
2	46·0	45·5	47·0
2½	46·0	45·4	46·0
20	45·9	45·3	46·1

Although damp cotton, on account of its swollen condition, dissolves more rapidly than dry it was found necessary to allow 4 hours dissolution time for the preparation of a ½ per cent solution. However, by preparing a solution of about half of this concentration the dissolution could be accomplished within 2 hours. The complete method, using about ¼ per cent solutions, was then tested on a series of damp cottons and the recalculated values for ½ per cent concentration compared with those obtained by the normal technique. It is inferred from Table VI that a reasonable agreement obtains over the range of fluidities considered.

This method is of course applicable to air-dry cottons, but the minimum times of dissolution then become 3 and 6 hours, respectively, for solutions of ¼ and ½ per cent concentration.

Table VI

Method	Fluidity at ½ per cent concentration							
Method 2	3·5	2·8	2·9	3·2	2·8	3·2	3·7	4·5
Control	2·7	2·9	3·0	3·0	3·1	3·4	3·8	4·0
Method 2	4·4	5·8	5·8	10·4	9·8	10·8	10·0	—
Control	4·1	6·1	6·9	9·6	10·2	10·4	10·5	—
Method 2	8·6	12·0	10·0	11·1	12·6	10·9	10·2	
Control	10·7	11·0	11·1	11·1	11·1	11·6	11·7	
Method 2	10·8	11·6	12·2	11·6	16·2	17·9	—	
Control	11·8	12·2	12·2	13·0	14·2	17·9	—	

APPENDIX

Details for construction of the nomogram.

In the formula $(f_0/f)^{1/6}-1=p\,c$ a value of 70 was assumed for f_0. Clibbens and Little (*loc. cit.*) gave 72 reciprocal poises as the mean value for the fluidity of the solvent.

The following two equations then hold simultaneously

$$(70/f_c)^{1/6}-1=p\,c$$

$$(70/f_{\frac{1}{2}})^{1/6}-1=p\,\tfrac{1}{2}$$

where $f_{\frac{1}{2}}$ is the fluidity, f_c, when $c=\frac{1}{2}$.
Eliminating p and taking logarithms

$$\log F(f_{\frac{1}{2}})-\log F(f_c)+\log c+\log 2=0$$

$$\text{where } F(f_c)=(70/f_c)^{1/6}-1.$$

This equation typifies a nomogram of three parallel straight lines and the constructional data were found by the usual method of determinants.

The information provided below refers to a rather larger diagram than Fig. 1.

The axes A and C commence at the same horizontal level, the distance between the axes A and B is 4 in.; the distance between the axes B and C is 6 in.

The following data give coarse graduations for the scales.

Scale A

Fluidity	3	4	5	6	7	8	9
Distance from A (ins)	0·00	0·62	1·16	1·62	2·02	2·40	2·74
Fluidity	10	12	14	16	18	20	22
Distance from A (ins)	3·07	3·66	4·20	4·74	5·21	5·68	6·12
Fluidity	24	26	28	30	32	34	36
Distance from A (ins)	6·59	7·00	7·46	7·88	8·31	8·78	9·25
Fluidity	38	40	42	44	46	48	50
Distance from A (ins)	9·66	10·22	10·67	11·22	11·71	12·31	12·90

Scale C

Concentration	0·1	0·15	0·2	0·3	0·4	0·5	0·6
Distance from C (ins)	0·00	3·17	5·42	8·59	10·84	12·58	14·01

Scale C can be further subdivided with the help of any simple logarithmic scale such as a slide rule

Scale B

This is graduated by finding the intersections of lines drawn from the point on scale C representing 0·5 per cent concentration to all the values on scale A

ACKNOWLEDGEMENT

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REFERENCES

[1] Clibbens, D A, and Geake, A *J Text Inst*, 1928, **19**, T77

[2] Clibbens, D. A, and Little, A H *J Text Inst*, 1936, **27**, T285

[3] Ridge, B P, and Bowden, H *J. Text. Inst*, 1932, **23**, T319

[4] Wannow, H A *Kunstseide u Zellwolle*, 1942, **24**, 144

[5] White, W A S, and Richardson, T N *J Text Inst*, 1944, **35**, T53

[6] Womersley, J R *J Text Inst*, 1935, **26**, T165

[7] Farrow, F D, and Neale, S M *J Text Inst*, 1924, **15**, T157

[8] Fabrics Co-ordinating Research Committee "The Viscosity of Cellulose Solutions," H M S O, 1932

[9] Doering, H *Papier Fabrikant*, 1940, **38**, 80

[10] Howlett, F, Martin, E, and Swan, J *J Text Inst*, 1946, **37**, T77

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26—AN ELECTRONIC INSTRUMENT FOR MEASURING WEIGHT VARIATIONS IN SLIVERS, ROVINGS AND YARNS

By G. N Boyd

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1. INTRODUCTION

Variations of weight and thickness having a roughly wave-like character are known to occur in spun yarn over distances of a few inches At the same time, changes in mean weight of longer lengths are also found to exist. Quantitative evaluation of the magnitude and form of the irregularities in yarns and slivers is important in the pursuit of experimental studies on drawing and spinning Suitable equipment for measuring variability is also valuable for control purposes in the mill This value has become more evident and important as a result of recent developments in yarn manufacture, particularly worsted yarn, where emphasis is being placed on the possibilities of reducing the number of operations involved.

One principle employed in several designs of instrument for measuring variation along the length of a yarn or sliver involves passing the material between metal shoes, a lower one in fixed position and an upper one responding to changes in thickness Movement of the upper shoe is suitably magnified and recorded Photoelectric methods have also been used in which yarn is passed in front of an illuminated slit and a measure of the light interference recorded Instruments depending upon change in resistance of a mercury column with change in cross-sectional area of a yarn have also been attempted, and recently a method depending upon changes in air-flow through a capillary tube caused by variations in size of yarn passing through the tube has been reported.

In all these methods the variation being measured is a change in thickness of the material or a change in the volume of a certain short length In some instances such data on yarn may be of direct value as for example in relation to visual appearance in a finished cloth' For most purposes, however, and particularly in connection with research on drafting, the most useful information to possess is a record of variation in weight This fact has been emphasized and fully discussed by Martindale,[1] and it need only be pointed out here that no simple correlation of diameter or volume measurements on yarn with weight exists The measurement of weight variation, however, has proved to be a matter of some difficulty In certain work requiring such data the method of cutting and weighing successive short lengths of material has been used The method is undesirable on account of its destructive nature, and is, in general, impractical in view of the very high consumption of time

In reviewing the requirements of a satisfactory instrument for measuring weight variation it was considered essential that the results provided should be a continuous record of weight change having reference to a suitable short length of material (*e g* 2 cm), and that the test should be non-destructive so that further drafting of the material could be carried out if necessary It was also considered desirable for a single instrument to be capable of handling materials over a wide range of weight and for measurements to be made reasonably rapidly and easily, so that an inexperienced person could readily be taught to conduct tests

One of the first instruments designed to measure weight variations continuously and in a manner non-destructive of the test specimen was described by Matthes and Mangartz,[2] in which the change in capacity of a condenser was measured as yarn or sliver was made to pass through it. In 1943, Dr. L. H. Turl working in these laboratories developed and constructed a recording instrument based on the same principle using an essentially similar type of electronic circuit to that employed by Matthes and Mangartz. As a result of experience gained with this instrument, further work was later undertaken with a view to improving the stability of the electronic circuit,

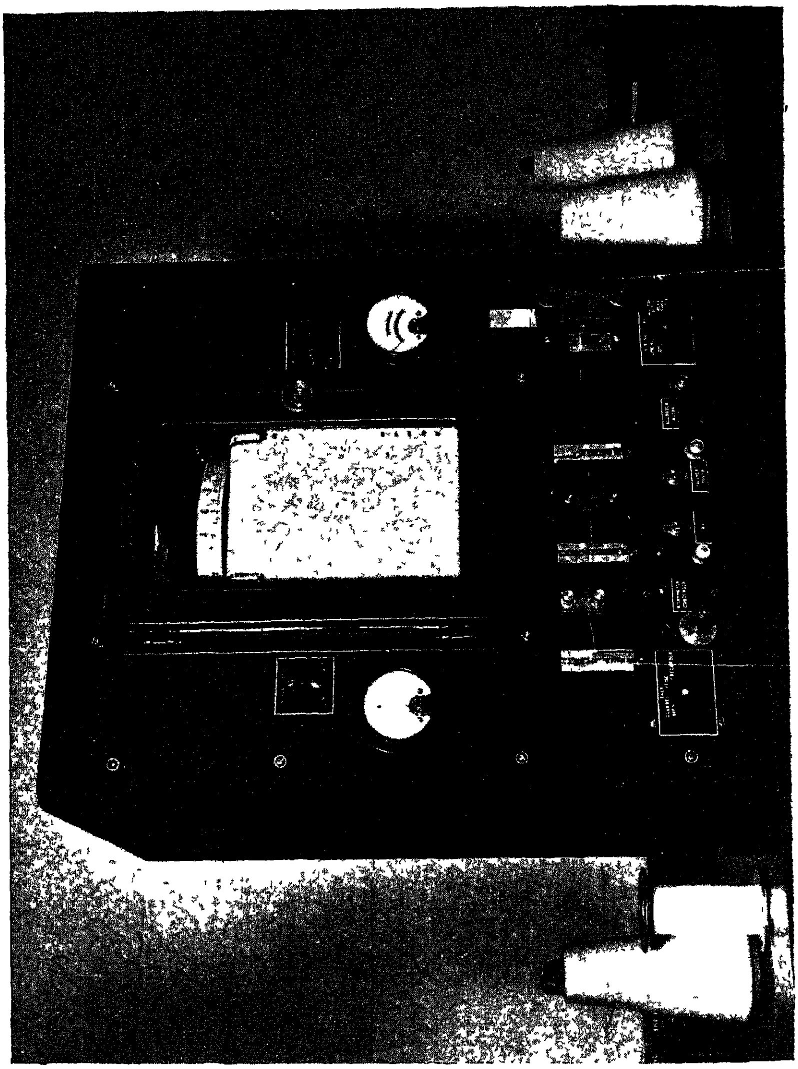

Fig. 1

particularly under adverse operating conditions of widely fluctuating line voltage. In the course of this further work, while the basic principle of measuring weight variation by change in capacity of a condenser was retained, the equipment was completely re-designed both electrically and mechanically. Desired improvements were successfully introduced, and the new design of instrument has now been operating for some time with satisfactory results both in the laboratory for research purposes and in the mill on control applications The general construction of the instrument and description of the circuit is recorded here together with information on the method of operation Some typical records are illustrated and a simple method of analysis which has been found useful is outlined.

2. DESCRIPTION OF THE INSTRUMENT AND CIRCUIT

If a substance having a different dielectric constant from that of air is introduced between the plates of a condenser the capacity of the condenser will change dependent upon the dielectric constant of the material, the amount introduced, and its shape or form In the case of relatively loose fibrous compositions such as yarns and slivers a choice of condenser can be made such that the change in capacity is so nearly in direct proportion to the weight of material between the plates that it can be taken as linear without introducing any serious error This fact will later be given experimental verification in the discussion of some results, and a theoretical treatment of the matter is given in Appendix I Actually the linear relationship is not essential to the method of measurement, but it is of great convenience in the analysis of records

In the instrument to be described the signal from a high frequency oscillator is used, after amplification, to generate a voltage across the tuned grid circuit of a detector This circuit is detuned from peak resonance so that a linear portion of the tuning curve is being used The voltage generated depends on the capacity of the measuring condenser through which the material is being passed The detector output voltage is recorded on a chart, and since it is proportional to the voltage generated in the tuned grid circuit, it is therefore a record of the change in weight of the material passing through the measuring condenser

A more detailed description of the instrument can most conveniently be given by reference to Figures 1, 2 and 3 which show, respectively, a front view photograph of the actual instrument, the panel layout, and the electrical circuit diagram Component parts are identified on the diagrams and in the text by letters and subscripts. Detailed description of these components, including electrical dimensions, tolerances, types and other pertinent information is given in Appendix II To facilitate consideration of the circuit different sections have been blocked in on the circuit diagram by distinguishing lines The construction of the instrument will be discussed under the headings (*a*) Mechanical, (*b*) High Frequency Measuring Unit, (*c*) Recorder Unit, (*d*) Circuit Checking Unit

(*a*) *Mechanical* The material to be tested is passed through a guide G_1 and then led under a tension block T B which has adjustable spring pressure and permits application of a suitably light tension In the case of top or heavy sliver, a U-shaped guide is employed From the tension block T B the material passes through the measuring condenser C_{11} which has guides G_2 and G_3 situated close to each end These latter are vertically adjustable in order to lock a suitable size of guide in line with the space between the condenser plates For heavy slivers, guides G_2 and G_4 are not used and the material is held in the measuring condenser by two U-shaped non-conducting rods inserted into the insulating condenser base plate at each end of the condenser A horizontal guide bar G B conducts the material into the nip of a pair of neoprene covered steel rollers D R , whose function is to draw the material through the condenser at a suitable uniform speed The inner roller of the pair is positively driven by the motor D M. and pressure between the rollers is adjustable through a pair of springs From the rollers D R the material passes over a polished guide strip G S , and may be wound onto a reel or allowed to fall into a suitable container

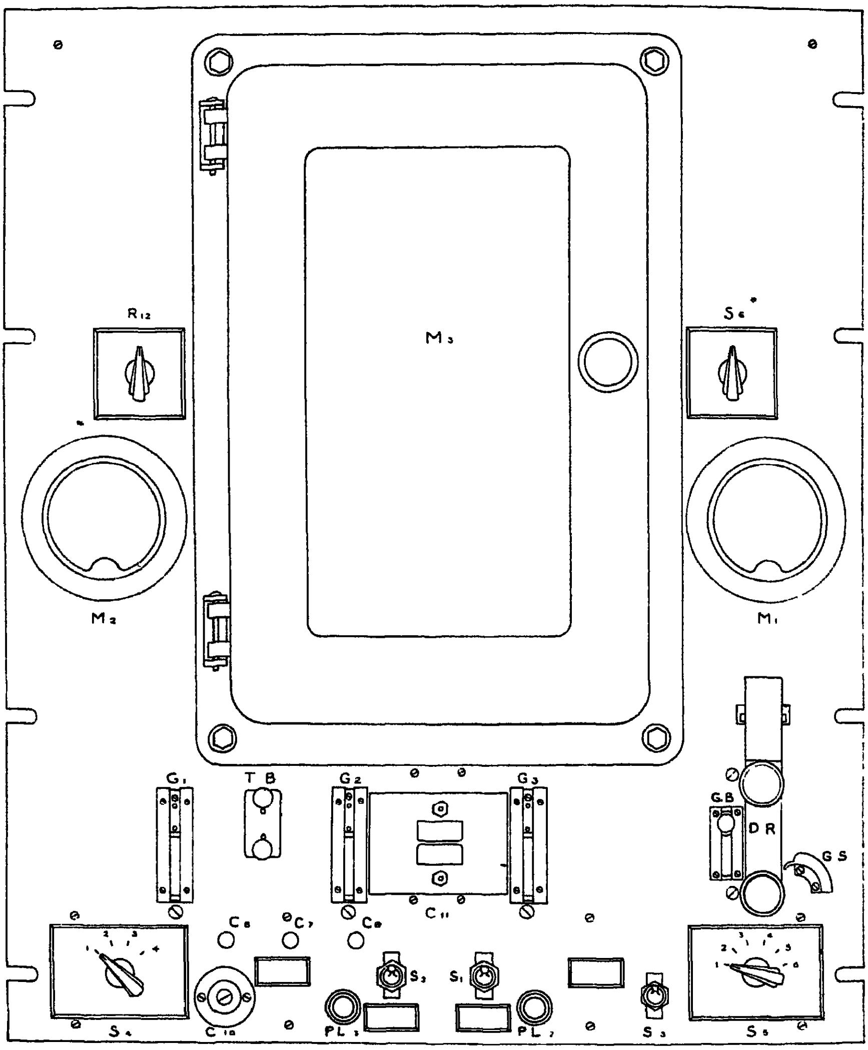

Fig 2

The motor D.M , which can be started through switch S_3, is a variable speed motor with built-in reducing gear In addition to driving the rollers D R. it is also made to drive the recorder chart which may be disconnected if desired by means of switch S_6 The speed of the recorder chart may be varied for a constant driveshaft speed by means of a set of change gears within the recorder itself. The ratio of driveshaft speed to the speed of the rollers D R may also be varied by a set of change-gears located just behind the panel In most cases it is desirable to have the material being tested travelling considerably faster than the chart so that the plot of weight variation is suitably condensed Practical ratios of material speed to chart

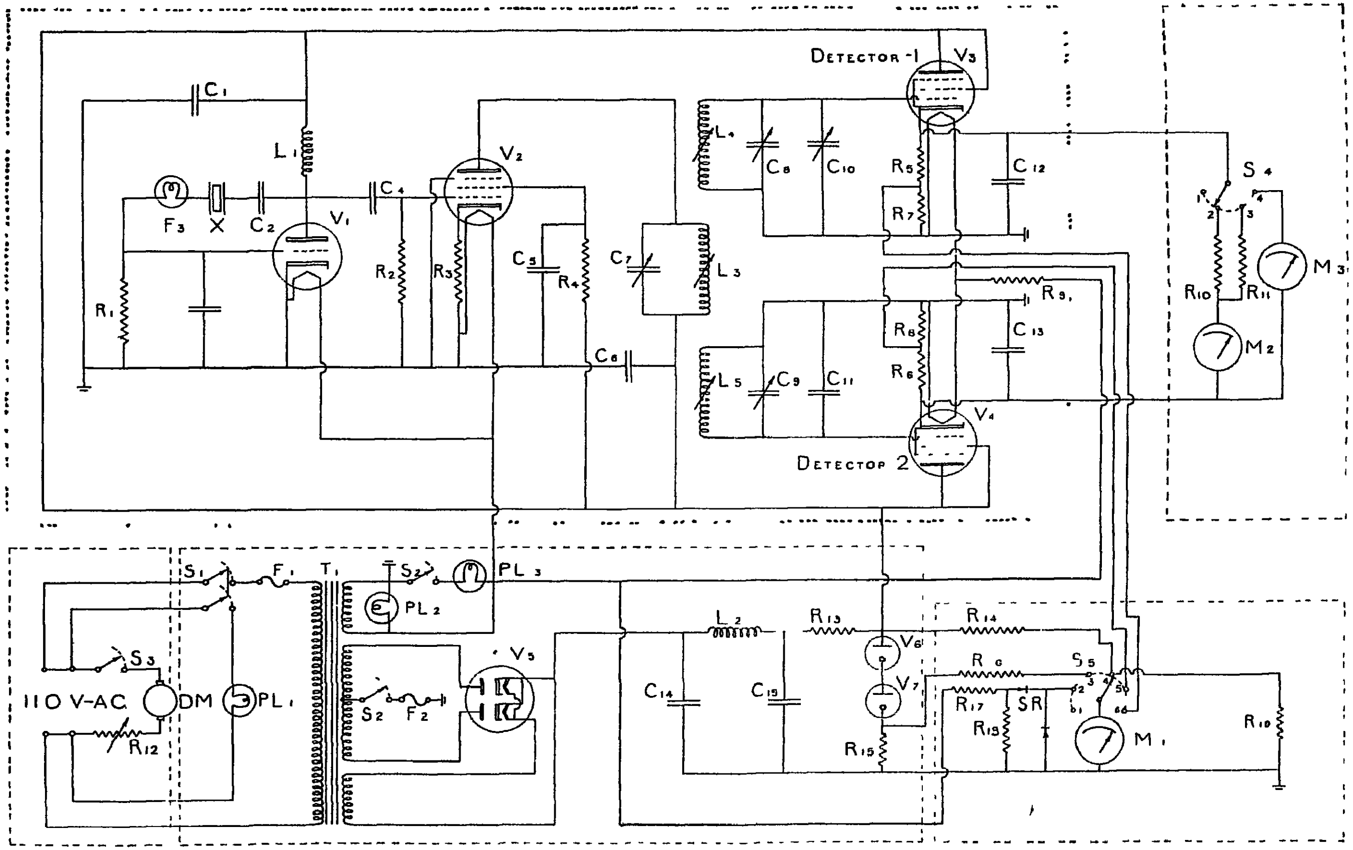
Detector -1
V3
C1
L1
V2
C4
F3
X
C2
V1
R1
R2
R3
C5
R4
C7
L3
C6
L4
C8
C10
R5
R7
C12
L5
C9
C11
R8
R6
R9
C13
V4
Detector 2
S4
1
2
3
4
R10
R11
M3
M2
S1
F1
T1
S2
PL3
PL2
S3
110 V-AC
DM
PL1
R12
V5
S2
F2
L2
R13
V6
R14
C14
C15
V7
R6
S5
R17
SR
R18
R15
M1
R10

Fig. 3

speed employed are 10.1 down to 1.1, although ratios even lower as well as higher are readily possible

The over-all speed of the whole unit may be varied continuously between zero and maximum by varying the motor speed through the use of rheostat R_{12} This does not, of course, affect the ratio of material to chart speed, but simply governs the speed of passage of material through the measuring condenser The time for the pen to move from its zero position to full scale deflection and back is one second, and is therefore correspondingly higher for smaller deflections Since the shortest periodic weight changes likely to be encountered have a minimum value of about two inches, a maximum speed for passage of material through the condenser was set at 20 ft per min

The measuring condenser C_{11} must be chosen so that no material protrudes beyond the edges of the plates and a mean deflection of approximately half full scale is obtained on the recorder This is readily achieved by the use of interchangeable condensers which plug into sockets on the panel and by making the spacing between the plates adjustable Since only four separate condensers have been found necessary to measure all materials from 15 denier nylon monofilament to wool top it requires but little experience to make a proper selection

(*b*) *The High Frequency Measuring Unit* The high frequency measuring unit is the portion shown in Figure 3 blocked in by a single dotted line It consists of the following stages a high frequency oscillator, a buffer amplifier, and two symmetrical detector stages

Valve V_1 is used in a crystal controlled Pierce type oscillator circuit which generates a 10 megacycle voltage A buffer amplifier stage incorporating valve V_2 is connected to the oscillator through condenser coupling The buffer stage amplifies the high frequency voltage generated by the oscillator to nearly 200 volts, and it also isolates the oscillator from any reflected impedance effects occurring in the later stages The tuned load of the buffer stage, C_7 and L_3, is adjusted to peak resonance, and through loose coupling it supplies high frequency voltage to each of the tuned grid circuits of the so-called infinite impedance detector stages The tuned circuit of detector 2 consists of inductance L_2 in parallel with the variable condenser C_9 and the measuring condenser C_{11} through which the yarn or other material is passed The tuned circuit of detector 1 consists of inductance L_1 in parallel with the variable condenser C_8, and the micrometer condenser C_{10} for fine adjustments. With the exception of condensers C_{10} and C_{11}, both of which actually represent a small portion of the total capacity in their respective circuits, the two detector tuned circuits are identical This, of course, results in both having sensibly identical resonance curves

The detector stages are both operated with their input circuits detuned from peak resonance so that a linear portion of the resonance curve is used in each case The value of the D C. output voltage for each detector stage at the midpoint of the range over which this linear condition exists was determined experimentally These two output voltages are almost exactly equal since the detector stages are as identical as possible in every respect. With no material in the measuring condenser, and for any setting of C_{10}, condensers C_8 and C_9 are adjusted until the D C output voltages from the detector stages are approximately equal to their proper experimentally determined values The output of detector 1 is then made exactly equal to that of detector 2 by adjustment of the micrometer condenser C_{10}

When the material under test is placed between the plates of the measuring condenser the capacity of the condenser changes Since the high frequency voltage across the detector tuned circuits varies linearly with the capacity in the circuits over the portion of the resonance curves used, and since the D C. voltage output from the detectors is directly proportional to the high frequency voltage input, it follows that the D.C voltage change occurring at detector 2 is directly proportional to the capacity change of the measuring condenser Because a linear relationship exists between capacity and weight, this voltage change is therefore a measure of the weight of the material between the plates The D C output voltage of detector 1, which is actually used as a reference voltage, remains substantially constant since the high frequency voltage input to the stage does not vary appreciably during the test The recorder measures the difference between the D C voltages produced by the two detectors, and therefore as the material is drawn through the measuring condenser this recorder reading indicates directly the weight of the material between the condenser plates at any instant

There are several advantages of using a balanced type circuit in the detector stages Variations in high frequency voltage output from the buffer stage, caused by variations in plate supply voltage, affect each detector stage equally The result is that such changes produce no change in the D C voltage difference which is being measured Further, since the same voltage is applied to the plates of both detectors, changes in the D C output voltages of the detectors due to changes in plate voltage tend to cancel one another Another advantage of the balanced circuit is that the filament voltages may be left unregulated Changes in the H F voltage output of the buffer amplifier due to filament voltage variations affect each detector equally In the detector stages themselves the problem is not quite so simple. If the detector valves have different emission characteristics, their D C. output will not vary by equal amounts as the filament voltage varies This effect is marked by a slow drifting of the voltage reading on the recorder. The drifting effect has been greatly reduced by careful matching of the detector valves for emission characteristics and by reducing the filament voltage applied to them by the common dropping resistor R_9

(*c*) *The Recorder Unit.* The recorder unit, shown blocked in on Figure 3 by an alternately dashed and dotted line, consists of two parts: the recorder itself, and a 0 to ±500 microamp galvanometer M_2, which is used for zero adjustments in order to protect the recorder With no material in the measuring condenser, the galvanometer is switched into the circuit across the detector cathode resistors by means of multi-throw switch S_1. Condenser C_{10} is adjusted until the galvanometer M_2 reads zero, first on a coarse scale with switch S_1 in position 2, and then on a fine scale by turning to position 3 By moving S_1 to position 4, the recorder M_3, an Esterline-Angus 0-10-20V recording voltmeter, is then introduced into the circuit

(*d*) *The Power Supply* The power supply, shown in Figure 3 enclosed by a single dashed line, is a very simple regulated type Since the output stage of the high frequency measuring unit consists of a balanced type circuit, close regulation of the plate supply voltage is unnecessary There are no controls to be adjusted by the operator for this power supply, since it produces only a single fixed plate supply voltage of 210 volts. Sufficient regulation is achieved by placing two VR 105 voltage regulator valves (V_6 and V_7) in series across the output of a standard supply and tapping the plate supply voltage from the plate of V_6. The power supply will maintain a 210 volt output to within ±5 volts for variations in A.C line voltage between 95 and 135 (The instrument was designed to operate on a normal line voltage of 110 volts, but with a suitable choice of power transformer T_1 it could be made to operate on any other voltage)

(*e*) *Circuit Checking Unit* This unit is shown in Figure 3 blocked in by a double dashed double dotted line It consists essentially of a D C meter M_1 which has a 1 ma full scale deflection, and may be connected by multi-throw switch S_5 through suitable dropping resistors to points in the circuit where voltage or current checks should be made before the instrument is used. Position 2 of switch S_5 gives a reading on meter M_1 of line voltage In this circuit the voltage from the filament winding of the transformer, which is normally a fixed proportion of the line voltage, is applied across the voltage divider R_{17} R_{18} The A C. voltage across R_{18} is half rectified by the selenium rectifier S.R , and the resultant voltage is applied to meter M_1 One scale of the meter is calibrated to convert this deflection directly to A C line voltage Position 3 of S_5 shows the current through the voltage regulator valves With switch S_5 in position 4, the meter M_1 reads plate supply voltage Here the meter is connected across R_{19}, part of the voltage divider R_{11} R_{19} which is connected across the plate supply voltage output The meter scale is calibrated to read plate voltage directly If the reading is not 210 ±5 volts the voltage regulator valves are not operating properly and their current must be checked Positions 5 and 6 of S_5 give meter readings of D C. volts across a section of the cathode resistors of the detector stages The scale is calibrated to read detector output voltage Using this scale these voltages are set at their proper operating point which, of course, means that they are at the same time roughly equalized before the more sensitive meter M_2 is used in conjunction with C_{10} for exact equalization

3. OPERATION OF THE INSTRUMENT

To operate the instrument, the filament voltage supply is first turned on by switch S_1 followed by turning on the plate voltage switch S_2 A warm-up period for the valves of about an hour is then advisable to avoid excessive drifting over long runs, although for testing short lengths of material for the variability within them this time may be considerably reduced Where the instrument is in daily use, for example, for plant control purposes, it is better for the power to be left on continuously rather than to be switched on and off more than once a day Such continuous operation is not harmful to the instrument and the inconvenience from zero drift during the warm-up period is virtually eliminated A suitable measuring condenser is selected and plugged in on the panel and, using M_1, the D C detector voltages are adjusted by means of condensers C_8 and C_9 until they are approximately equal and so that linear portions of the detector tuned circuit resonance curves are being used. The voltages are then equalized very exactly by using the micrometer condenser C_{10}, first in conjunction with the coarse scale of meter M_2 followed by use of the fine scale The recorder is then switched into the circuit and will, of course, be found to read zero

The material to be tested is threaded through the proper guides, and inserted into the measuring condenser If necessary, the spacing of the plates is adjusted to give about half scale deflection on the recorder Movement of the plates, of course, unbalances the previous zero setting and condenser C_{10} must be readjusted to compensate With a little practice the whole adjustment process can be carried out in a few minutes

The fact that the measuring condenser plate spacing is adjusted to obtain a suitable mean deflection when the sample is inserted, in no way affects the irregularity record of the sample Since the response of the device may be considered linear, a larger mean deflection simply results in larger deflections from the mean. The ratio of a given deflection from the mean (due to a change in weight of the material) to the mean itself is always constant If an absolute value for the mean is desired it is necessary only to weigh a suitable length of specimen, but where uniformity is the sole consideration absolute values of weight are not required

At the end of a test or at any time during a run, in order to be sure that no drift has occurred a check of the zero can readily be made by allowing the material to by-pass the measuring condenser and observing the reading on the galvanometer M_2

Because the dielectric constant of a fibre is influenced to a very marked degree by moisture content, it is essential that material to be tested should be in a uniform moisture condition This does not normally present any serious difficulty even for control work in the mill, because in any range of moisture content likely to be encountered in practical operation, provided this moisture content within the material to be tested is uniform, the ratio between variations from the mean and the mean itself is substantially unaffected The possibility of any difficulty arising from variable moisture content is, of course, completely obviated by conditioning and examining of material in a room of controlled humidity and temperature

4. SOME EXPERIMENTAL RESULTS AND TYPICAL RECORDS

(*a*) *Linearity Test* It was previously stated that the change in capacity of the measuring condenser is very closely in direct proportion to the weight of textile material between the plates If this, for any reason, were not the case, or if the detector characteristic curve were not linear, the recorder reading would increase for unit increases in weight of material according to some curve, and this would have to be determined for calibration purposes Such a test can be simply performed by inserting between the plates of the condenser a successively increasing number of lengths of some uniform material and observing the recorder reading

Undrawn nylon yarn was chosen because of its very high degree of uniformity The plates of the measuring condenser were spaced so that when a single end of the yarn was inserted it produced a reading of approximately 2 volts on the recorder which has a full-scale reading of 10 volts Ten readings were taken over a short length of each of five ends of yarn tested separately and the average of the 50 measurements was taken as the mean reading for the single end of yarn Five readings were then made on each of the ten combinations of two yarns and a like number on each of the ten combinations of three yarns Ten readings were taken on each of the five combinations of four yarns and finally fifty measurements made on the five yarns taken together The average of the fifty readings in each case was taken to represent the value for the particular group and these values are shown plotted in Figure 4 It can be seen that the curve is sufficiently close to being linear that for practical purposes it may be so regarded

(*b*) *Some Typical Records* In Figure 5 are shown portions of records made of three widely different products In all cases the ratio of speed of material to chart speed was 10 1 and the portions of the records shown represent about 10 ft of material Record 5(a) is that of a single end of 64s botany sliver taken after the first drawing operation on a set of French drawing At this stage the sliver weight was 4 5 oz per 10 yards, very similar to that of the top from which it was prepared. The short term irregularities, which can be seen occurring over what are roughly 4 inch intervals, are of relatively small magnitude. Evidence can also be seen of an irregularity repeating over longer distances In Figure 5(b) is shown a portion of a record of a 1/20s worsted yarn spun according to conventional mill practice from the same lot of wool as the sliver shown in 5(a) The yarn received eight operations of French drawing followed by mule spinning The increased amplitude of the short period variations is strikingly apparent and shifts in the mean weight over longer lengths may also be noted Figure 5(c) is a portion of a record made of 15 denier nylon monofilament, the chief point of interest being the high degree of uniformity of this material.

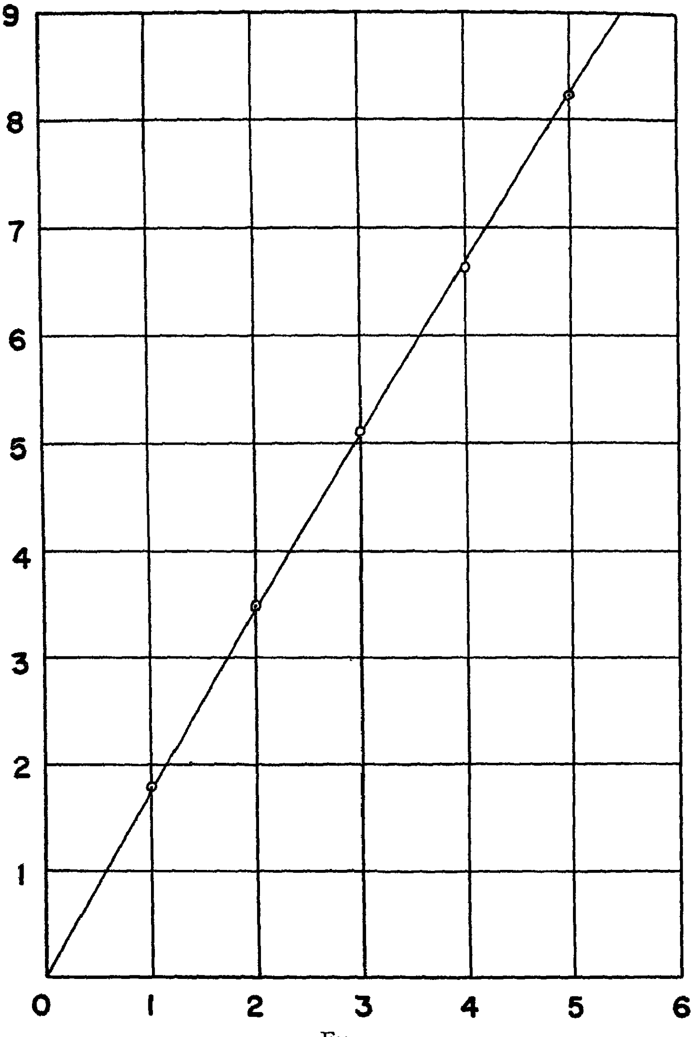

Fig 4

So far as the electrical circuit is concerned, there is virtually no limit to the size or weight per unit length of material which can be measured Mechanical considerations on the present design of instrument, however, limit the size of materials which can conveniently be handled A wool top represents the approximate upper limit, while the nylon monofilament shown in Figure 5(c) indicates the approximate lower limit (*c*) *Examination of Records* The data extracted from these records depend, of course, on the use to which they are to be put If it is desired to express the weight distribution of a material by a mean and standard deviation or by any other set of descriptive statistics, the records may be converted to frequency distributions and the requisite computations made These calculations are somewhat lengthy. Furthermore, for many purposes, they conceal rather than exhibit the most important features of the records. This, because all variations, both short term and long term, are thrown inextricably together in the frequency distribution

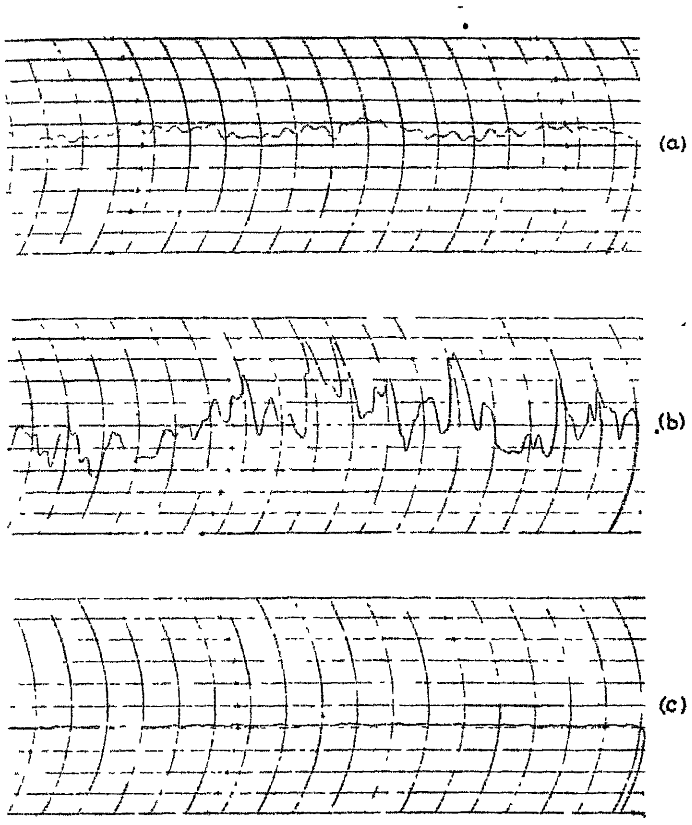

Fig 5

The following method of analysis, which has been found particularly useful for purposes of plant control, permits a measure to be made of both short and longer term variations in a simple and rapid manner The records are divided into unit sections of equal length, using a distance somewhat greater than the shortest predominant irregularity cycle An average of the maximum and minimum readings in each section is taken, and these values are themselves averaged over the whole record This over-all average yields a close estimate of the mean weight of the material. If a record is divided into a number of suitably long portions, the average deviation of the means of these portions from the over-all mean shows long term variations. The difference between maximum and minimum readings in each unit section is also recorded These individual differences are averaged, and this average difference is expressed in terms of the mean weight of the material This provides a measure of the short term variations

More informative and detailed analyses which find application in connection with studies in drafting are being given attention

ACKNOWLEDGEMENTS

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REFERENCES

[1] Martindale *J Text Inst*, 1945, 36, T35
[2] Matthes and Mangartz *Textilberichte*, 1940, 21, 326

APPENDIX I

Mathematical Consideration of Capacitance

The relation between the capacity of a parallel plate condenser and the quantity of material interposed between the plates may be considered mathematically in the following manner

Let A be the area of each of the two condenser plates,
L the distance between the plates,
V the volume of material interposed between the plates,
K the dielectric constant of this material, and
C the capacity of the condenser

Regard reference axes x, y as lying in the plane of one of the plates Across the distance L from one plate to the other, the perpendicular from a point x, y on one of the plates will pass through air and interposed material Let the total length of material traversed by this perpendicular be $u(x,y)$ Then the capacity of the elemental condenser with plate dimensions dx, dy is given by

$$\frac{dx\,.\,dy}{4\pi\left(L-u+\frac{u}{K}\right)}$$

For convenience put $\rho=1-\frac{1}{K}$ and the above expression may be written

$$\frac{1}{4\pi L}\cdot\frac{dx\,dy}{1-\rho\,\frac{u}{L}} \qquad (1)$$

The capacity C of the whole condenser is therefore given by integrating over the total area of the plate, or

$$\begin{aligned} C &= \frac{1}{4\pi L}\iint\frac{dx\,dy}{1-\rho\cdot\frac{u}{L}} \\ &= \frac{1}{4\pi L}\iint\left(1+\rho\frac{u}{L}+\rho^2\cdot\frac{u}{L}+\;.\;\;.\;\;.\right)dx\,dy \\ &= \frac{A}{4\pi L}+\frac{\rho V}{4\pi L^2}+R \qquad . \qquad (2) \end{aligned}$$

$$\text{where } R=\frac{1}{4\pi L}\iint\sum_{i=2}^{\infty}\rho^i\left(\frac{u}{L}\right)^i dx.dy \tag{3}$$

It can be seen that if the value of u/L is everywhere sufficiently small, the value of R is small and the relation between C and V is effectively linear In the case of loosely packed material such as wool tops and lightly twisted slivers this condition obtains At later stages of processing the value of u/L may be fairly large, as for example in yarn where the spinning twist has been inserted The most critical case for such yarn which can be formulated for examination appears to be when the diameter of the yarn is equal to the distance between the plates

The condenser plates are rectangular, of length a and width b, and the yarn lies in the condenser parallel to the sides of length a The yarn may be assumed to be circular in cross-section and its diameter is L the distance between the plates Let λ be the proportion of the cross-sectional area of the yarn actually occupied by fibre To simplify the integration imagine a new set of reference axes, x, y lying in a plane parallel to the condenser plates midway between them with the origin at the midpoint of a line joining the centre points of the plates The x axis is taken to be parallel to the side b of the condenser plate and the y axis parallel to the side a Let the longitudinal centre axis of the yarn coincide with the y axis The integral giving the capacity of the condenser may now be evaluated

$$C=\frac{1}{4\pi L}\int_{-\frac{a}{2}}^{\frac{a}{2}}\int_{-\frac{b}{2}}^{-\frac{L}{2}}dx\,dy+\frac{1}{4\pi L}\int_{-\frac{a}{2}}^{\frac{a}{2}}\int_{-\frac{L}{2}}^{\frac{L}{2}}\frac{1}{1-2\rho\lambda\left(\frac{\sqrt{(L-2)^2-x^2}}{L}\right)}dx\,dy+\frac{1}{4\pi L}\int_{-\frac{a}{2}}^{\frac{a}{2}}\int_{\frac{L}{2}}^{\frac{b}{2}}dx\,dy$$

$$=\frac{a(b-L)}{4\pi L}+\frac{a}{4\pi L}\int_{-\frac{L}{2}}^{\frac{L}{2}}\frac{dx}{1-2\rho\lambda\left(\frac{\sqrt{(L-2)^2-x^2}}{L}\right)}$$

Making the substitution $x=\frac{L}{2}\sin\theta$, and $dx=\frac{L}{2}\cos\theta\,d\theta$, then

$$C=\frac{a(b-L)}{4\pi L}+\frac{a}{4\pi L}\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}}\frac{(L-2)\cos\theta\,d\theta}{1-2\rho\lambda\frac{L}{2}\cdot\frac{\cos\theta}{L}}$$

$$=\frac{a(b-L)}{4\pi L}+\frac{a}{4\pi\rho\lambda}\left[\frac{2}{\sqrt{1-\rho^2\lambda^2}}\tan^{-1}\sqrt{\frac{1+\rho\lambda}{1-\rho\lambda}}-\frac{\pi}{2}\right] \tag{4}$$

The extent to which C varies with λ can be given more precise meaning by substituting in equation (4) appropriate numerical values for a, b, L and K The dimensions of the condenser plates used for yarns are $a=1{\cdot}0$ in ; $b=0$ 1 in The distance apart of the plates may be taken to be $L=0{\cdot}01$ in. which corresponds to what is normally used for a 1/30s worsted yarn. The exact value of K is dependent upon the particular fibre and its moisture content Reasonably wide variations in this value from sample to sample may take place without materially influencing the relationship between C

and λ. It is necessary, of course, that K remain constant within each sample. A value for K equal to 5 is taken here for purposes of calculation.

The first term of equation (4) is constant and is the contribution to the capacity of those portions of the measuring condenser which lie beyond the edges of the sample. Using the values for a, b, L and K given above this term (C') is equal to 0·7162, and of course does not in any way affect the shape of the curve relating C to λ. In Table I are given the values for the second term (C'') for values of λ over the full range 0 to 1, together with the figures for the total capacity C. Column 4 gives the first order differences and serves to show the departure from linearity at the higher values of λ. The curve of C against λ is illustrated in Figure 6.

Table I

λ	C''	C ($=C'+C''$)	Δ
0·0	0·07958	0·79578	—
0·1	0·08505	0·80125	0·00547
0·2	0·09113	0·80733	0·00608
0·3	0·09846	0·81466	0·00733
0·4	0·10721	0·82341	0·00875
0·5	0·11777	0·83397	0·01056
0·6	0·13102	0·84722	0·01325
0·7	0·14816	0·86436	0·01714
0·8	0·17124	0·88744	0·02308
0·9	0·20456	0·92076	0·03332
1·0	0·25792	0·97412	0·05336

Change in capacity is due only to change in λ, and it is to be seen that for values of λ up to 0·4 or 0·5 the relationship is very nearly linear. A λ greater than 0·5 would probably only be encountered in the case of a monofilament, where λ=1. Under these conditions the departure from linearity would be quite marked. In other types of yarn, the value of λ would seldom exceed 0·5 and would generally be considerably lower. For the extreme case therefore where the yarn has a diameter sufficient to touch both condenser plates the relationship between C and λ is reasonably linear, except in the case of monofilaments. For yarn whose diameter is less than L, but has the same value for λ, the ratio u/L is less, and in this case the relationship between C and λ would be more linear than that shown in Figure 6. Where monofilament is being tested, it is possible to obtain sufficient recorder deflection even though the condenser spacing is considerably greater than the filament diameter. This results in a relatively low value of u/L, and compensates to some extent for the high value of λ involved.

In the above argument, variations in quantity of material interposed between the condenser plates have been treated as variations in λ, or what is the same thing as variations in bulk density. At the opposite extreme where the bulk density remains constant, the square of the diameter of the yarn is proportional to the weight or quantity of material present. Consider a typical yarn where λ is 0·3 or 0·4 and the mean diameter is somewhat less than the condenser plate spacing. It follows that the value of u/L is considerably less than 0·3 or 0·4. It is obvious from equation (3) that the R term, whose size is governed by the u/L ratio, is very small, or in other words that the capacity-volume relationship is almost linear. If the bulk density of this yarn remains constant but the weight increases by 50 per cent the diameter will increase by a factor of about 1·2. With a constant λ the function $u(x,y)$ increases directly as the diameter, and since L is always constant the u/L ratio also increases as the diameter As the R term was very small before the 50 per cent increase in weight, the increase by 1·2 in the u/L ratio will not be sufficient to affect materially the linear relationship between C and V

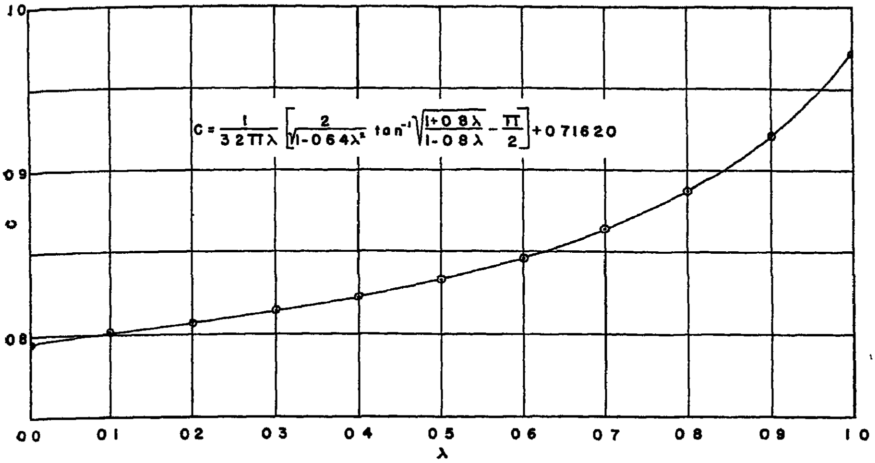

Fig 6

In actual fact the variations in weight along a yarn are accompanied by variation both in cross-sectional area and in bulk density, and earlier investigations reported in the literature have indicated that such weight variations are reflected fairly closely by a linear change in diameter rather than by the square of the diameter In this case an increase in diameter must be accompanied by a corresponding decrease in bulk density which results in the u/L ratio remaining unchanged This implies that regardless of weight variation R remains very small, and therefore the relation between C and V is always sensibly linear.

It has been shown that changes in fibre volume are reflected directly by changes in capacity for the following four cases.

(1) top or sliver where the u/L ratio is always very small,
(2) yarn whose diameter is constant and for which λ varies within any practical limits,
(3) yarn for which λ is constant and where the diameter varies within practical limits,
(4) yarn for which λ and diameter both vary

It will of course be obvious that for material of uniform composition, fibre volume is equivalent to weight

APPENDIX II

The symbols used in the following list correspond with the designations given to component parts in the panel and circuit diagrams (Figures 2 and 3), also referred to in the text

Abbreviations	mfd	microfarad
	mmfd	micro-microfarad
	D C W V.	direct current working voltage
	mh	millihenries
	amp	amperes
	ma	milliamperes
	max	maximum
	D P S T	double pole single throw
	S P S T	single pole single throw
	S P 4 T	single pole four throw

Parts

Symbol	
	CONDENSERS
C_1, C_2, C_6, C_{12}, C_{13}	0 01 mfd —600 D C W V —mica
C_3	50 mmfd —600 D C W V —mica
C_4	20 mmfd —600 D C W V —mica
C_5	0 005 mfd —600 D C W V —mica
C_7, C_8, C_9	0-35 mmfd —air dielectric—variable
C_{10}	0-1 mmfd —air dielectric—variable
C_{11}	Interchangeable measuring condenser—air dielectric—variable (see note)
C_{14}, C_{15}	8 mfd —600 D C W V —electrolytic
	RESISTORS
R_1	100,000 ohms—±10%—1 watt—type F (see note)
R_2	50,000 ohms—±10%—1 watt—type F (see note)
R_3	68 ohms—±10%—1 watt
R_4	22,000 ohms—±10%—2 watts
R_5, R_6	100,000 ohms—±10%—1 watt
R_7, R_8	40 ohms—±10%—0 5 watt
R_9	0-10 ohms—±10%—wire wound—adjustable
R_{10}	250,000 ohms—±10%—1 watt
R_{11}	10,000 ohms—±10%—1 watt
R_{12}	0-225 ohms—±10%—50 watt—wire wound—adjustable
R_{13}	4,000 ohms—±5%—100 watt—wire wound
R_{14}	200,000 ohms—±10%—1 watt
R_{15}	10 ohms—±10%—1 watt
R_{16}	400 ohms—±10%—1 watt
R_{17}	3,300 ohms—±10%—1 watt.
R_{18}	2,200 ohms—±10%—1 watt
R_{19}	200 ohms—±10%—1 watt
	INDUCTANCES
L_1	3 mh high frequency choke
L_2	10 Henry—150 ma choke
L_3	Adjustable high frequency choke—powdered iron core (see note)
L_4, L_5	High frequency chokes (see note)
	TRANSFORMERS
T_1	Primary input =70 volt amps Secondary output =375 volts—100 ma max with 110 volt primary input Filament windings (*a*) 5 volt—2 amp max (*b*) 6 3 volt—3 amp max
	FUSES
F_1	250 volts—2 amp —instrument type fuse
F_2	250 volts—0 5 amp —instrument type fuse
F_3	2 volts—50 ma max bulb
	SWITCHES
S_1	D P S T toggle switch
S_2	D P S T toggle switch
S_3	S P S T toggle switch
S_4	S P 4 T rotary switch
S_5	S P 6 T rotary switch
S_6	Gravity release recorder clutch switch
	VALVES
V_1	6J5 oscillator triode
V_2	6AG7 buffer amplifier pentode
V_3, V_4	6K6-G detector pentodes
V_5	5V4-G full wave high vacuum rectifier
V_6, V_7	V R 105 voltage regulators
	PILOT LAMPS
PL_1	110 volt, 60 ma
PL_2, PL_3	6 volt, 250 ma
	METERS
M_1	0 0-1 0 ma D C milliameter.
M_2	—0 5—0 0+0 5 ma D C milliameter
M_3	—0—10—20 volts—Esterline Angus recording D C voltmeter milliameter No 49921
	MISCELLANEOUS
SR	5 ma selenium rectifier
X	10 mc Bliley-type M021 crystal—temp 25° C
DM	Universal wound motor 1/50 H P, 10,000 r p m at 110 volts—built in gear reducer with ratio 595 1

NOTE —No specific value of capacity is listed for measuring condenser C_{11} because this actually consists of a set of three interchangeable condensers The smallest, which is used to test fine yarns has plates 1 0 cm long and 0 32 cm wide With a plate spacing of 0·013 cm which is that used to obtain a suitable deflection of the recorder when testing 1/56s worsted yarn for example, the capacity of the condenser is approximately 2 mmfd The change in capacity of this condenser on insertion of the yarn is only a portion of 1 mmfd The other measuring condensers have plates 2 0 cm long the smaller being 0 64 cm wide the larger 1 92 cm wide In the case of the largest measuring condenser the plate spacing used when testing wool top for example, is of the order of 0 6 cm which means that before insertion of the top this condenser has a capacity considerably less than 1 mmfd. However, since there is so much more textile material in a cross section of the top than there is in a cross section of the yarn, the net capacity change in both condensers is about the same on insertion of the textile material, and this change is a small fraction of a mmfd The same argument applies also to the intermediate measuring condenser The capacity of the measuring condensers is only a small fraction of the total capacity of its resonant circuit, since the variable condenser C_9 is set at about 25 mmfd to obtain a D C output of 150 volts from the measuring condenser detector tuned circuit. Because of this fact any dielectric losses occurring in the measuring condenser due to insertion into it of the textile material have negligible effect on the shape of the resonance curves They may always therefore be considered sensibly identical

Type F resistors, such as R_1 and R_2, are often used in high frequency applications The resistor consists of a hollow ceramic tube on the inside of which is sprayed or painted a layer of carbon which constitutes the actual resistance The ends are metal caps with the usual lead out wires

No specific values of inductance have been determined for L_3, L_4 and L_5, but other information about them may be useful They are wound on three Bakelite formers 1 5 inches long, 0 5 inches in diameter and with a 0 25 inch diameter threaded hole running axially through the centre of each former Into the centre of the middle former was threaded a 0·5 inch long powdered iron tuning slug The three formers are joined together by means of short polystyrene plugs threaded into the axial centre holes, so that effectively a single 4 5 inch long former is used This former is mounted about 1 inch below the chassis in a plane parallel to the top by means of Bakelite and supports The primary coil L_3, is wound on the centre former using 23 turns of 24 enamelled copper wire The secondary coils, L_4 and L_5, are wound on the outside formers so that they are symmetrically placed with respect to the primary, and the centre to centre distance between primary and secondary coils is 1 43 ± 0 06 inches Each secondary coil consists of 28 turns of 24 enamelled copper wire The two secondary tuned circuits are sufficiently loosely coupled to one another, so that changes of several volts in the measuring condenser detector tuned circuit result in changes of less than 0 1 volts in the micrometer condenser detector tuned circuit

F_3, listed as a fuse, is actually a very low current bulb which lights up when the oscillator is in operation Thus it serves both as a fuse which guards against excessive high frequency current from passing through the crystal, and also as an indicator

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27—ALKALINE SCOURING OF DRY SPUN FLAX YARNS: EFFECT UPON PHYSICAL PROPERTIES OF YARN AND FABRIC

By H. L PARSONS

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The boiling or scouring of heavy, dry spun, flax yarns in aqueous alkaline solutions has been practised for many years as an important item in the production of heavy or mechanical fabrics such as tent ducks, tarpaulins, and canvasses which have to withstand continuous outdoor usage This boiling or "wasting" as it is often called in the trade, is carried out to varying degrees of loss in weight in order to reduce subsequent loss in weight on "weathering" and to improve resistance to microbiological decay

It is already well-known that retted flax (and also true hemp), in their commercially available forms, consist chemically of approximately 65 per cent high quality (*i e* long chain length) cellulose, 14-17 per cent hemicellulose and pectin, 8-11 per cent moisture and smaller amounts of protein, mineral ash, wax and water-soluble matter Alkaline scouring dissolves, or otherwise removes, much of the non-cellulosic matter, the actual loss in weight depends upon the type of flax, the time and temperature of scouring, liquor ratio and the type and concentration of alkali used It is a matter of general experience that caustic soda removes more weight in boils of 3-5 hours' duration and tends to produce more wettable yarns than those obtained with soda ash when used under similar conditions Various retted flaxes give appreciably different losses in weight when subjected to any one scouring treatment whilst unretted or "natural" flax—obtained from flax straw by purely mechanical decortication—gives considerably higher losses in water and in alkaline solutions than retted flaxes similarly treated

Gibson, Nodder and Lynch of the Linen Industry Research Association first examined the scouring of dry spun flax yarns in relation to the measurement of residual alkali-soluble matter and elaborated the so-called Alkali Solubility Test * This useful technique, which is now widely used as a measure of the chemical purity of flax yarns, consists simply of the determination of the loss in weight, expressed on oven dry weights, both in water and 5 per cent soda ash solution The loss in water subtracted from the loss in alkali is termed the ***alkali solubility number***. This test, although arbitrarily standardised, does serve as a good criterion of the efficiency of boiling as regards the final chemical purity of the yarn

Elkin[1] has shown that the general graphical relationship existing between loss in weight on boiling and residual alkali solubility number is of the sigmoid type. By the use of a modified form of the Searle[2] rotting technique, Elkin showed that resistance to microbiological decay increased as alkali solubility number fell, although resistance to rotting did not appear to increase much between the alkali solubility number range 10 per cent. down to 5 per cent For a given alkali solubility number, yarns boiled in caustic soda appeared less rot-resistant than those boiled in soda ash liquor It is known that the major part of the non-cellulosic matter—pectin, hemicellulose, water-soluble matter and protein—provide more easily accessible nutrient for micro-organisms and permit these to grow under favourable conditions of moisture and warmth until they reach a state sufficiently active to attack the cellulose itself Removal of these foodstuffs reduces susceptibility to decay.

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* The Alkali Solubility Number test should not be confused with the Solubility Number test also devised by the Linen Industry Research Association for measuring the degree of chemical attack of flax materials

The value placed upon yarn boiling in the dry spun flax trade is reflected in its inclusion in many modern specifications for heavy fabrics as used by the Services, Railways and Shipping Companies throughout the world

EXPERIMENTAL

Various dry spun flax yarns were spun to such counts (or grists) that after boiling to the required loss in weight, the final grists were all nominally the same at 4¾ lb /sp. (10s lea) warp and 10 lb /sp (4 8s lea) weft Three types of flax, namely, retted tow, retted line and unretted (or natural) line were used, whilst all the yarns in any one series were spun from the same flax mix The boiling range covered residual alkali solubility numbers of grey, 15 per cent , 10 per cent , 5 per cent and 2 per cent (nominal) Warps and wefts were, in each case, woven into fifteen fabrics of the same construction, *i e* 22-23 oz /sq yd., 26 double warp threads per inch, 23 weft threads per inch , and were finished identically in all respects Boiling of the yarns was done by the usual bulk method using soda ash and caustic soda to achieve the desired losses in weight

TESTING TECHNIQUE

A. Grey Unboiled Yarns

Grist Dry spun flax yarns are expressed in the grist system, namely lb weight per spyndle of 14,400 yards

Six hanks, each of six cuts, were chosen at random from each spin and were conditioned at 65-70 per cent R H at 70° F for at least 24 hours Two 100-yard grist test hanks were then reeled off in such a manner that an equal portion of each original cut was included, and were weighed to the nearest 0 1 gram Grist was then calculated and thus twelve grist tests of truly representative nature were obtained The mean and coefficient of variation were calculated This C V figure is, of course, always much less than that obtained on shorter lengths, *e g* 1 yard or 1 inch, but is looked upon more as a measure of gristing constancy than of yarn weight or diameter variability

Tensile Strength Thirty conditioned specimen lengths (36 inches) were taken from each of half the grist hanks in such a manner that five tests were, in effect, from each cut of the six cut original hank, *i e* 180 tests were done on each type of yarn The average strength and the coefficient of variation were then calculated The other six grist hanks were then steeped in cold tap water at room temperature (70° F) for one hour and were tested in a similar manner to the conditioned hanks A Goodbrand tester, constant rate of traverse 12 inch/minute, of range 0-10, 0-50 lb was used throughout for all yarn strength tests

Twist Twenty determinations on 10 inch lengths were made on each of the six original hanks and the average and C V were calculated

B. Boiled Yarns

Loss in Weight due to Scouring. The remainder of the six original hanks from each spin were conditioned, weighed and then sent to the bleachfield, where they were included in bulk in various positions in the pot change After passing through the appropriate processing they were returned to the laboratory for reconditioning and weighing

Grist and Twist, were determined as for the grey yarns

Tensile Strength Similar strength tests on the conditioned and saturated boiled yarns were done as for the grey yarn In addition ten strength tests on one inch lengths of yarn, both conditioned and saturated, were done on each of the six grist hanks, *i e* sixty tests were done, in each state, on each yarn

Table I. Grey Yarns

No	CONDITIONED					SATURATED			Q_{sat}/Q_{cond} 36"	Twist T P I	Twist C V %
	Grist lb/sp	Grist C V %	Mean strength 36" lb	Quality number 36" lb /lb	Strength 36" C V %	Mean strength 36" lb	Quality number 36" lb /lb	Strength 36" C V %			
RT1 Warp	4 8	3 4	4 70	0 99	16 4	6 39	1 33	14 5	1 34	6 23	14 8
Weft	9 7	3 6	7 55	0 78	21 0	10 3	1 04	20 2	1 33	4 27	14 2
RT2 Warp	5 0	2 5	4 75	0 95	17 5	6 90	1 38	15 3	1 45	6 14	5 2
Weft	10 6	2 1	8 58	0 81	16 0	11 8	1 11	16 1	1 37	3 90	6 7
RT3 Warp	5 5	2 6	5 72	1 04	14 8	7 45	1 33	13 9	1 28	5 85	9 2
Weft	11 4	2 7	9 92	0 87	17 0	13 0	1 14	16 1	1 31	3 61	9 8
RT4 Warp	5 7	1 8	6 04	1 06	13 7	7 92	1 39	13 7	1 31	5 81	9 0
Weft	12 5	1 4	11 0	0 88	15 1	14 4	1 15	15 4	1 31	3 59	8 4
RT5 Warp	6 1	1 9	6 77	1 11	15 5	8 36	1 35	14 6	1 22	5 79	8 9
Weft	12 7	3 7	11 4	0 99	17 4	15 4	1 19	17 5	1 32	3 43	12 3
RL1 Warp	4 7	1 5	6 74	1 43	19 9	8 19	1 74	17 1	1 22	5 05	11 0
Weft	10 0	1 7	14 5	1 45	14 2	15 7	1 57	13 1	1 08	3 47	13 4
RL2 Warp	4 9	3 1	7 31	1 49	15 0	8 50	1 70	15 7	1 14	5 11	7 5
Weft	10 6	2 4	15 2	1 44	15 4	16 7	1 57	12 8	1 09	3 18	13 6
RL3 Warp	5 5	4 1	8 35	1 52	17 5	9 61	1 78	15 0	1 17	5 01	9 9
Weft	11 4	2 2	16 1	1 42	14 7	17 3	1 53	12 9	1 08	3 07	13 0
RL4 Warp	5 7	0 5	8 62	1 51	14 0	10 4	1 83	13 5	1 21	4 90	10 4
Weft	12 3	2 1	18 4	1 50	13 7	19 5	1 60	13 7	1 07	3 03	10 4
RL5 Warp	6 0	0 5	9 24	1 54	16 0	11 3	1 89	11 8	1 22	4 77	10 3
Weft	13 0	1 1	18 4	1 55	15 2	22 0	1 71	12 2	1 10	2 97	12 0
NL1 Warp	4 8	3 1	5 12	1 08	29 7	5 80	1 23	25 2	1 14	5 32	15 2
Weft	10 1	1 8	17 2	1 70	17 9	14 9	1 46	16 9	0 86	3 16	13 5
NL2 Warp	5 5	5 2	6 81	1 24	25 0	7 70	1 40	21 6	1 13	4 98	14 9
Weft	11 8	2 2	21 0	1 78	16 5	18 6	1 58	13 8	0 89	3 13	11 8
NL3 Warp	5 9	3 1	7 80	1 32	23 3	7 74	1 29	20 7	0 98	4 91	14 5
Weft	13 1	2 2	24 2	1 85	17 2	20 3	1 55	15 3	0 84	2 47	12 5
NL4 Warp	6 7	1 6	8 84	1 32	22 5	9 31	1 39	16 4	1 05	4 70	12 7
Weft	14 2	1 8	26 1	1 84	16 5	21 9	1 55	14 8	0 84	2 88	10 4
NL5 Warp	6 9	0 8	9 65	1 40	19 6	9 45	1 39	16 1	1 00	4 68	12 0
Weft	14 8	3 4	25 3	1 71	15 1	24 1	1 66	12 2	0 97	2 54	8 4

Grist=Yarn Weight in lb per 14,400 yards (Spyndle)

$$\text{Quality number}=\frac{\text{Mean yarn strength lb}}{\text{Conditioned yarn grist lb /sp}}$$

C V =Coefficient of variation %

T P I =Turns per inch

Fibre Strength and Extensibility at Break. Single fibre strength and extensibility tests were determined in the conditioned and saturated states by means of a Cambridge Extensometer

Alkali Solubility Number Two tests were made on well-mixed cuttings from each yarn, according to the standard technique laid down by the Linen Industry Research Association

Solubility in 5 per cent Caustic Soda Solution. The solubility or loss in weight referred to oven-dried boiled yarn weight incurred by boiling in 5 per cent caustic soda for 2½ hours was also determined

C Fabrics

After weaving, the pieces were cropped to remove loose fibre, and were measured for width, length and weight, and the weight in ounces per square yard was then calculated

Table II. Boiled Yarns

No	CONDITIONED					SATURATED			$\frac{Q_{sat}}{Q_{cond}}$ 36"	Twist TPI	Twist CV %
	Grist lb /sp	Grist CV %	Mean strength 36" lb	Quality number 36" lb /lb	Strength 36" CV %	Mean strength 36" lb	Quality number 36" lb /lb	Strength 36" CV %			
RT1 Warp Weft				N O	T	B O I	L E D				
RT2 Warp Weft	5 0 10 5	1 0 5 7	5 05 8 91	1 01 0 84	17 7 16 8	7 00 13 1	1 45 1 25	15 1 19 8	1 43 1 49	6 04 4 15	7 2 9 4
RT3 Warp Weft	5 1 11 1	1 6 2 4	5 75 11 2	1 13 1 01	15 0 15 8	8 00 14 3	1 57 1 31	14 7 17 9	1 39 1 30	5 90 4 13	8 2 11 1
RT4 Warp Weft	4 9 10 9	0 4 1 8	6 26 11 7	1 28 1 08	16 6 15 5	8 44 15 6	1 72 1 45	15 3 17 9	1 35 1 55	5 90 4 15	9 8 11 0
RT5 Warp Weft	5 0 10 4	1 6 3 7	6 95 11 8	1 39 1 13	14 8 17 4	9 35 18 0	1 87 1 68	14 7 17 9	1 35 1 49	5 86 3 96	8 3 8 5
RL1 Warp Weft				N O	T	B O I	L E D				
RL2 Warp Weft	4 9 10 5	2 2 1 2	7 25 14 3	1 48 1 36	15 1 15 7	9 35 17 8	1 95 1 71	15 0 13 8	1 36 1 26	5 08 3 26	10 8 9 0
RL3 Warp Weft	5 1 10 6	2 8 2 6	8 65 15 9	1 70 1 50	13 3 13 8	10 7 18 5	2 05 1 76	12 8 12 8	1 21 1 17	5 95 3 37	9 1 11 5
RL4 Warp Weft	5 0 10 6	1 1 2 0	9 56 17 8	1 91 1 68	14 4 15 5	11 6 20 8	2 31 1 97	13 9 13 2	1 21 1 17	4 93 3 03	9 5 11 8
RL5 Warp Weft	4 8 10 6	2 1 1 7	9 00 18 1	1 87 1 71	13 6 11 4	12 8 24 0	2 60 2 29	13 5 12 2	1 39 1 34	5 12 3 11	8 4 9 1
NL1 Warp Weft				N O	I	B O I	L E D				
NL2 Warp Weft	4 7 10 3	3 0 1 9	5 40 15 4	1 15 1 49	23 0 17 4	7 64 17 9	1 59 1 76	21 2 14 3	1 38 1 18	5 29 3 16	10 4 9 8
NL3 Warp Weft	5 1 10 9	2 8 1 7	7 70 18 0	1 51 1 65	17 9 16 0	9 30 20 2	1 86 1 83	18 4 13 1	1 23 1 11	4 86 3 14	8 1 8 9
NL4 Warp Weft	5 4 11 0	2 6 1 4	9 00 19 5	1 67 1 77	18 1 15 0	11 6 23 7	2 18 2 16	18 8 11 8	1 30 1 22	4 88 3 05	9 4 9 7
NL5 Warp Weft	5 2 11 0	1 9 2 2	8 45 19 0	1 62 1 73	19 7 16 1	12 6 24 3	2 42 2 21	17 9 13 1	1 50 1 28	5 04 2 95	11 0 11 0

Tensile Strength Six warpway and six weftway strips, 3 in. wide, were frayed down to one inch wide and were then tested in both the conditioned and saturated states, the distance between the jaws of the testing machine being seven inches The testing instrument used was a Goodbrand 1100 lb machine, constant rate of traverse 18 inches per minute.

Tear Strength Six tongue-tear tests across the warp and also across the weft were done in both the conditioned and the saturated states, on a constant rate of traverse machine

The measured data are recorded in Tables I to VI

Table III. Boiled Yarns

No	36" Mean strength ratio—Boiled/Grey		CONDITIONED			SATURATED			Q_{sat}/Q_{cond} 1"	Twist Boiled /Twist Grey
	Conditioned	Saturated	1" Mean strength lb	1" Q'ty number lb /lb	1" C V of strength %	1" Mean strength lb	1" Q'ty number lb /lb	1" C V of strength %		
RT1 Warp										
Weft				NO	T B	OILE	D			
RT2 Warp	1 06	1 01	8 10	1 62	18 2	10 8	2 16	16 9	1 33	0 99
Weft	1 04	1 11	13 3	1 27	21 4	18 2	1 73	19 9	1 36	1 06
RT3 Warp	1 00	1 07	8 55	1 68	18 0	11 3	2 22	13 6	1 32	1 01
Weft	1 13	1 10	15 7	1 41	23 2	19 7	2 18	17 7	1 54	1 15
RT4 Warp	1 04	1 07	9 00	1 84	21 3	11 4	2 24	20 0	1 22	1 02
Weft	1 06	1 08	17 5	1 61	20 5	22 4	2 06	23 9	1 28	1 16
RT5 Warp	1 03	1 12	10 0	2 00	15 2	13 9	2 78	15 2	1 39	1 01
Weft	1 03	1 17	20 2	1 94	16 0	23 0	2 21	15 6	1 14	1 16
RL1 Warp										
Weft				NO	T	BOI	LED			
RL2 Warp	0 99	1 10	11 5	2 35	19 8	13 2	2 70	22 0	1 15	1 00
Weft	0 94	1 07	17 3	1 65	19 2	18 6	1 77	19 8	1 07	1 02
RL3 Warp	1 04	1 11	11 0	2 16	16 6	13 5	2 65	14 0	1 23	1 01
Weft	0 99	1 07	22 6	2 14	17 1	25 5	2 41	19 1	1 13	1 10
RL4 Warp	1 11	1 11	11 7	2 34	17 5	15 2	3 04	19 2	1 30	1 01
Weft	0 97	1 07	22 6	2 13	16 7	25 3	2 39	21 5	1 12	1 00
RL5 Warp	0 98	1 13	13 3	2 77	19 3	17 7	3 68	15 2	1 33	1 07
Weft	0 99	1 09	22 8	2 16	15 7	27 3	2 58	21 0	1 20	1 05
NL1 Warp										
Weft				NO	T	BOI	LED			
NL2 Warp	0 79	0 99	9 32	1 98	28 4	11 4	2 43	21 5	1 23	1 06
Weft	0 73	0 96	21 6	2 10	17 3	23 9	2 22	17 6	1 05	1 01
NL3 Warp	0 99	1 20	13 0	2 54	20 3	14 2	2 78	19 8	1 09	0 99
Weft	0 74	1 00	21 1	1 94	20 4	19 2	2 00	16 8	1 03	1 27
NL4 Warp	1 02	1 25	12 0	2 22	25 5	15 1	2 80	18 2	1 26	1 04
Weft	0 75	1 08	24 5	2 21	15 2	26 0	2 36	15 7	1 07	1 06
NL5 Warp	0 88	1 33	12 8	2 46	23 2	18 8	3 62	19 5	1 47	1 07
Weft	0 75	1 01	23 6	2 14	21 5	30 6	2 78	16 9	1 30	1 16

Table IV. Boiled Yarns

No	Scouring weight loss %	Yarn moisture content %	Alkali solubility number %	N_A %	N %	FIBRE					
						Tensile Strength			Extension at break		
						Conditioned mean Kg/mm²	Saturated mean Kg/mm²	Sat / cond	Conditioned mean Kg/mm²	Saturated mean Kg/mm²	Sat / cond
RT1 Warp	Unboiled	7 1	12 4	22 6	32 8	101	115	1 14	4 4	2 2	0 50
Weft	-	7 9	12 5	20 1	32 8	—	84	—	—	2 4	—
RT2 Warp	3 2	6 8	13 0	17 8	23 6	70	106	1 51	3 2	3 6	1 13
Weft	3 7	7 2	11 8	17 7	26 2	57	38	0 67	2 2	4 0	1 82
RT3 Warp	6 5	7 7	11 0	14 2	24 7	88	70	0 80	5 2	9 0	1 73
Weft	6 4	8 0	10 6	13 6	25 6	90	64	0 71	6 0	14 8	2 46
RT4 Warp	13 5	7 6	5 5	6 7	16 6	89	79	0 89	6 2	(24 0)	(3 87)
Weft	9 7	7 8	4 4	6 3	16 8	77	43	0 56	4 4	10 4	2 36
RT5 Warp	19 3	6 7	1 5	2 5	10 9	112	87	0 78	2 8	3 6	1 29
Weft	19 0	6 7	1 6	2 5	11 7	60	63	1 05	5 2	3 0	0 58
RL1 Warp	Unboiled	8 2	13 0	18 8	33 8	—	82	—	—	6 4	—
Weft		8 8	12 2	18 4	34 0	88	78	0 89	5 1	9 0	1 77
RL2 Warp	2 3	8 6	12 9	17 0	29 9	—	44	—	—	9 5	—
Weft	3 3	8 8	13 8	19 2	32 4	58	53	0 92	6 0	6 4	1 07
RL3 Warp	6 5	7 5	11 1	14 0	25 0	—	60	—	—	2 1	—
Weft	5 9	7 4	11 6	15 2	27 6	111	87	0 78	3 0	5 2	1 73
RL4 Warp	13 1	7 3	5 1	6 5	16 7	111	99	0 89	10 6	2 0	0 19
Weft	14 4	7 7	4 3	5 6	17 1	89	63	0 71	2 2	4 2	1 91
RL5 Warp	19 3	6 7	1 0	1 8	11 1	116	100	0 86	2 2	5 7	2 59
Weft	19 8	6 6	1 9	3 1	12 1	78	57	0 73	7 0	10 6	1 51
NL1 Warp	Unboiled	9 6	12 4	35 4	50 0	86	116	1 35	11 2	4 0	0 36
Weft		8 5	12 0	33 2	50 0	90	30	0 30	3 6	8 0	2 22
NL2 Warp	11 7	8 5	13 8	18 0	30 6	52	62	1 19	10 0	7 6	0 76
Weft	13 3	8 2	12 6	16 3	33 5	55	53	0 97	3 0	4 6	1 53
NL3 Warp	15 8	7 7	11 5	15 1	26 3	57	66	1 16	4 0	4 4	1 10
Weft	17 2	7 1	9 1	12 1	28 2	32	30	0 94	4 8	7 4	1 54
NL4 Warp	20 4	7 5	6 1	8 9	19 5	59	69	1 17	11 2	6 2	0 55
Weft	21 4	7 1	5 7	7 3	20 8	78	58	0 75	5 6	5 6	1 00
NL5 Warp	25 1	7 1	1 5	2 6	12 1	80	34	0 43	4 0	5 2	1 30
Weft	30 8	6 5	2 4	3 6	13 9	45	85	1 89	4 6	3 6	0 78

N_A=Solubility or loss in weight in boiling 5% Soda Ash solution (2½ hours) expressed on residual insoluble matter

N=Alkali solubility as for N_A but using 5% Caustic Soda

Table V. Fabrics

No	Weight oz per sq yard	TENSILE STRENGTH								lb /in /oz Sat/cond ratio	Mean ratio
		Conditioned				Saturated					
		lb /in	Mean	lb /in /oz	Mean	lb /in	Mean	lb /in /oz	Mean		
RT1 Warp	22 7	243	269	10 7	11 8	343	374	15 1	16 5	1 41	1 39
Weft		295		13 0		405		17 8		1 37	
RT2 Warp	23 4	233	291	10 0	12 4	350	409	15 0	17 5	1 50	1 42
Weft		348		14 9		468		20 0		1 34	
RT3 Warp	23 8	247	312	10 4	13 1	379	448	16 0	18 9	1 53	1 46
Weft		376		15 8		517		21 8		1 38	
RT4 Warp	23 0	274	318	11 9	13 8	453	496	19 7	21 6	1 66	1 58
Weft		361		15 7		538		23 4		1 49	
RT5 Warp	23 2	283	356	12 3	15 3	443	525	19 1	22 6	1 57	1 50
Weft		429		18 5		607		26 2		1 42	
RL1 Warp	21 3	293	296	13 7	16 2	427	427	20 1	20 1	1 46	1 27
Weft		398		18 7		426		20 1		1 07	
RL2 Warp	22 8	315	409	13 8	18 0	467	548	20 5	24 0	1 48	1 37
Weft		503		22 0		629		27 6		1 25	
RL3 Warp	24 0	358	435	14 9	18 1	508	572	21 2	23 9	1 42	1 33
Weft		511		21 3		635		26 6		1 24	
RL4 Warp	23 6	376	453	16 0	19 2	492	607	20 9	25 7	1 31	1 34
Weft		530		22 4		721		30 6		1 36	
RL5 Warp	23 0	358	463	15 6	20 1	515	657	22 4	28 6	1 44	1 43
Weft		568		24 8		799		34 8		1 41	
NL1 Warp	21 5	293	443	13 6	20 6	337	411	15 7	19 2	1 15	0 99
Weft		590		27 4		484		22 6		0 82	
NL2 Warp	22 6	262	419	11 6	18 5	381	470	16 9	20 8	1 45	1·21
Weft		575		25 5		559		24 8		0 97	
NL3 Warp	23 7	301	438	12 7	18 5	436	565	18 4	24 0	1 45	1 33
Weft		575		24 3		694		29 2		1 21	
NL4 Warp	25 0	332	512	13 3	20 5	457	646	18 3	25 9	1 38	1 30
Weft		691		27 6		834		33 5		1 21	
NL5 Warp	24 4	338	498	13 8	20 5	488	672	20 0	27 5	1 44	1 37
Weft		658		27 0		853		35 0		1 30	

Table VI. Fabrics

No Across		TONGUE TEAR STRENGTH				Sat /cond. ratio
		Conditioned		Saturated		
		lb	Mean	lb	Mean	
RT1	Warp	127	115	139	136	1 18
	Weft	103		132		
RT2	Warp	113	101	145	137	1 35
	Weft	89		128		
RT3	Warp	117	110	161	148	1 34
	Weft	102		135		
RT4	Warp	117	118	154	154	1 30
	Weft	118		154		
RT5	Warp	114	115	164	165	1 43
	Weft	115		166		
RL1	Warp	146	157	162	156	1 00
	Weft	165		149		
RL2	Warp	141	144	177	167	1 16
	Weft	147		157		
RL3	Warp	151	147	177	178	1 21
	Weft	143		178		
RL4	Warp	149	151	175	174	1 15
	Weft	153		172		
RL5	Warp	147	168	190	212	1 26
	Weft	188		234*		
NL1	Warp	114	153	160	173	1 13
	Weft	191		185		
NL2	Warp	83	136	168	196	1 44
	Weft	189		224*		
NL3	Warp	114	155	173	196	1 26
	Weft	195*		218*		
NL4	Warp	92	133	227*	234	1 76
	Weft	173		241*		
NL5	Warp	106	139	191	216	1 55
	Weft	172		240*		

* Measured on 1,100 lb capacity Goodbrand machine, others measured on 200 lb machine

DISCUSSION OF RESULTS

Yarn Grist

Both grey and boiled yarns are substantially steady at the grists expected The average figures for grist variation taken upon 100 yard lengths (CV) over all grey and over all boiled yarns are ±2 8 per cent and ±2 2 per cent respectively, whilst there is also little or no indication that the coefficient of variation changes as grey grist increases within the range studied

Yarn Tensile Strength

(*a*) *Yarn Actual Mean Strength* (36 *inch test lengths*).

The mean ratios over all warps and wefts in each series for mean yarn tensile strength in the boiled state divided by that in the grey state have been calculated from the figures in Table III thus—

Table VII

Fibre	Ratio of Mean Yarn Strength (36″) Boiled to Mean Yarn Strength (36″) Grey	
	Conditioned	Saturated
Retted Flax Tow	1·05±0·014	1·09±0·017
Retted Flax Line	1·00±0·019	1·09±0·036
Natural Flax Line	0·83±0·043	1·10±0·049

It is concluded within the range and type of dry spun flax yarns studied that alkaline scouring tends to increase slightly the tensile strength of retted tow yarns, to have no effect on retted line yarns, and tends markedly to decrease the tensile strength of yarns spun from natural or unretted flax line, all in the conditioned state. In the state saturated with water, however, the tensile strengths of all yarns appear, on the average, to increase by roughly 9 per cent when boiled. Warp and weft yarns behave similarly and there is no indication that severity of boiling has any effect. The plus and minus figures are standard errors of the means in each case.

(*b*) *Yarn Quality Number* (36 *inch*.)

The quality number provides a convenient method for comparing yarn strengths, irrespective of yarn grist, and is defined as follows—

$$\text{Quality number (lb./lb.)} = \frac{\text{mean yarn strength (lb.)}}{\text{mean yarn grist (lb./sp.)}}$$

i.e the quality number of dry spun flax yarns is the strength (lb.) per lb. of grist. Hence as yarn grist falls, due to loss in weight on boiling, quality number will tend to rise irrespective of any change in yarn strength. Where losses in weight are known, an expected increase in quality number may be calculated and compared with the change actually found. Any difference between these two figures will be due to change in yarn strength.

As would be expected, there is a general tendency for the quality number to rise for any one flax mix as yarn grist increases in the grey conditioned state. This is shown by the means of warps plus wefts over the five grist sets taken thus—1·24, 1·28, 1·34, 1·35, 1·38 lb./lb. Taking appropriate averages to clarify matters we have—

Table VIII

Data	Retted Tow		Retted Line		Natural Line	
	Warp	Weft	Warp	Weft	Warp	Weft
Grey Conditioned Quality Numbers	1·03	0·85	1·50	1·47	1·27	1·78
Grey Saturated Quality Numbers	1·38	1·13	1·79	1·60	1·34	1·56
Ratio Sat./Cond.	1·34	1·38	1·20	1·09	1·05	0·88
Boiled Conditioned Quality Numbers	1·20	1·02	1·74	1·56	1·49	1·66
Boiled Saturated Quality Numbers	1·65	1·42	2·23	1·93	2·01	1·99
Ratio Sat./Cond.	1·38	1·39	1·28	1·23	1·35	1·20

In the unboiled conditioned state the natural line wefts have the highest intrinsic strength, due in some measure to the high grey grist employed to give requisite grist after boiling The weakest yarns are the retted tow wefts Upon saturation, remarkable differences are observed; thus the yarns spun from retted flax tow increase roughly by the same amount—36 per cent —the retted line yarns increase by roughly 20 per cent for warps and 9 per cent for wefts whilst the natural line warps increase only by 5 per cent The natural line wefts actually decrease by 12 per cent

For the boiled yarns in the conditioned state all warp yarns are roughly of 4¾ lb /sp in grist and all weft yarns stand nominally at 10 lb /sp Here the retted line warps are strongest and retted tow yarns are weakest Upon saturation all the boiled yarns increase in quality number, once more the retted tow yarns show the greatest percentage increase, whilst the natural line wefts show the lowest Whilst the fundamental causes responsible for this difference in behaviour remain to be elucidated, it is suggested that in these measured data lies some knowledge which might be utilised for the identification of various flaxes when in the form of dry spun yarn

It will also be noted for all yarns (Table II), that as the severity of boiling increases to give a constant final grist from yarns of increasing grey grist, *i e* the greater the content of *alkali-insoluble* matter or the greater the chemical purity of dry spun flax yarns, the greater is the conditioned quality number or intrinsic yarn tensile strength The same observation applies for dry spun flax yarns when saturated with water From previous extensive experience in the effect of boiling techniques of varying severity, the author suggests that their effect upon any one yarn of any one grist should not be materially different from the deductions obtained from this present work

(*c*) *Coefficient of Variation of Yarn Strength* (36 *inch.*)

Once more calculating suitable averages we have—

Table IX

Data	Retted Tow		Retted Line		Natural Line		Mean
	Warp	Weft	Warp	Weft	Warp	Weft	
Grey Conditioned	15 6	17 3	16 5	14 6	24 0	16 6	17·4
Grey Saturated	14 4	17 1	14 6	12 9	20 0	14 6	15 6
Boiled Conditioned	16 0	16 4	14 1	14 1	19 7	16 1	16 1
Boiled Saturated	15 0	18 2	13 8	13 0	19 1	13 1	15 4
Mean	15 3	17 3	14 8	13 7	20 7	15 1	

It is concluded that the retted line yarns tend to be most regular in strength, whilst the natural line warps are least regular due possibly to under-gristing, *i e.* forcing the fibre to spin below its optimum minimum grist In both the grey and boiled states saturation tends to decrease slightly yarn strength irregularity. Boiling also tends to reduce irregularity to a minor extent.

(*d*) *Yarn Quality Number* (*1 inch*)

Table X

Data	Retted Tow		Retted Line		Natural Line	
	Warp	Weft	Warp	Weft	Warp	Weft
Boiled Conditioned	1·78	1·56	2·41	2·02	2·30	2·10
Boiled Saturated	2·35	2·05	3·02	2·29	2·91	2·34
Sat /Cond Ratio	1·32	1·32	1·25	1·14	1·27	1·12
Cond 1″/Cond 36″ Ratio	1·48	1·53	1·38	1·29	1·54	1·26
Sat 1″/Sat 36″ Ratio	1·42	1·44	1·35	1·18	1·45	1·17

$$\frac{\text{Mean Conditioned Quality Number } 1''}{\text{Mean Conditioned Quality Number } 36''} = 1{\cdot}41$$

$$\frac{\text{Mean Saturated Quality Number } 1''}{\text{Mean Saturated Quality Number } 36''} = 1{\cdot}34$$

Although the figures are somewhat erratic, it is concluded that the effective increase of yarn tensile strength due to decrease of specimen length from 36 inches down 1 inch is slightly higher in conditioned than in the saturated state The individual increases appear to be related to the type of fibre used.

(*e*) *Single Fibre Strength* (*Kg /sq mm*)

Table XI

Data	Retted Tow		Retted Line		Natural Line		Mean
	Warp	Weft	Warp	Weft	Warp	Weft	
Boiled Conditioned	90	71	114	84	62	53	—
Boiled Saturated	86	52	76	65	58	57	—
Sat /Cond Ratio	0·96	0·73	0·67	0·77	0·94	1·07	0·86

The erratic nature of the individual figures renders the drawing of exact conclusions difficult The tendencies exist, however, for retted fibre to be stronger than unretted and for retted line to be stronger than retted tow

Saturation with water tends to reduce the strength of flax fibre Averaging strength values over all boiled and all grey fibres in both the conditioned and saturated states also appears to show that boiling reduces flax fibre strength slightly (average grey 88 kg /sq mm , average boiled 73 kg /sq mm) The mathematical relationship between yarn strength and fibre properties may be expressed in its simplest form thus—

$$S = \frac{K.F.L}{\sqrt{A}} \text{ where } S = \text{Yarn strength,}$$

F=Fibre strength,
L=Mean fibre length,
A=Mean fibre fineness,
K is a constant

The proportionality constant K includes terms related to internal friction, twist, regularity, *etc.* The general marked increase in flax yarn strength when wetted and yet the simultaneous reduction in fibre strength must mean that K increases since it is unlikely that L or A can be effected by saturation It is generally accepted that the pronounced lateral swelling which occurs when flax fibres are wetted will increase fibre to fibre binding or internal friction

(*f*) *Single Fibre Extensibility at Break per cent*

Table XIA

Data	Retted Tow		Retted Line		Natural Line		Mean
	Warp	Weft	Weft	Warp	Warp	Weft	
Boiled Conditioned	4·4	4·5	(6·4)	4·6	7·3	4·5	5·1
Boiled Saturated	10·1	8·1	4·8	6·6	5·9	5·3	6·8
Sat./Cond. Ratio	2·30	1·80	—	1·43	0·81	1·18	1·33

The individual figures are too erratic to permit the drawing of exact conclusions, but it seems that a definite tendency exists for saturation to increase elongation at break. Evidence of a more tenuous character exists which shows that elongation increases very slightly upon scouring.

The single tensile strength figure quoted by Meredith[3] for conditioned unboiled line flax, *viz.* 6·1 gm./den. or 83 kg./sq. mm. is somewhat lower than the over-all average calculated above (88 kg./sq. mm.) His value of 3 per cent. for elongation at break is also lower than the over-all average value recorded here (5·1 per cent.).

Twist

Boiling has a slight, but definite, increasing effect upon yarn twist. The increase is similar for retted tow and natural line yarns and rather larger than for retted line.

Fibre	Ratio of Boiled Yarn Twist to Grey Yarn Twist
Retted flax tow	1·07
Retted flax line	1·03
Natural flax line	1·08

Loss in Weight on Boiling and Residual Alkali Solubility

The alkali solubility technique devised by the Linen Research Association as a measure of the chemical purity of boiled flax yarns has gradually become looked upon as an inverse measure of the probable loss in weight which has occurred during scouring. It has therefore been used as an aid to the bleacher who has to scour the yarns, and by the analyst who has to report upon, not only the chemical purity, but also the probable wastage in order that a suitable grey grist may be calculated for the spinner.

Figure 1 shows losses in weight incurred during boiling plotted against residual alkali solubility. The retted tow and line points appear to lie about one curve and the natural line points about another roughly parallel but displaced in the direction of greater loss in weight for equal alkali solubility. The complexity of these curves prevents any simple formula from being obtained as an analytical aid, but it is suggested that a simple relation should exist if the testing technique aimed at determination of the total soluble matter as distinct from that due to the alkali alone. It is further desirable that the boiling conditions used in the test should be more severe than anything likely to be met with in bulk practice.

Mathematically, the relation between weight loss on scouring and residual solubility may be expressed as follows—

Consider 100 parts oven dry grey flax containing S_0 parts soluble matter under the severest scouring conditions, and hence $(100-S_0)$ parts insoluble matter.

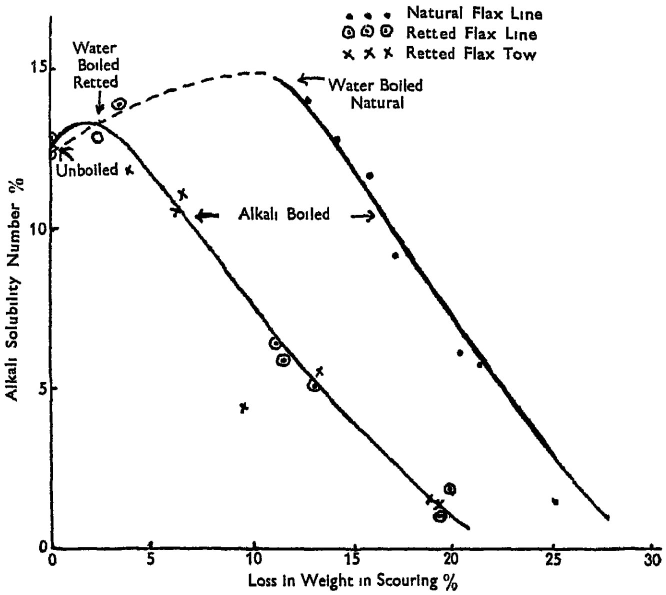

Fig 1

Loss in weight on scouring and alkali solubility number.

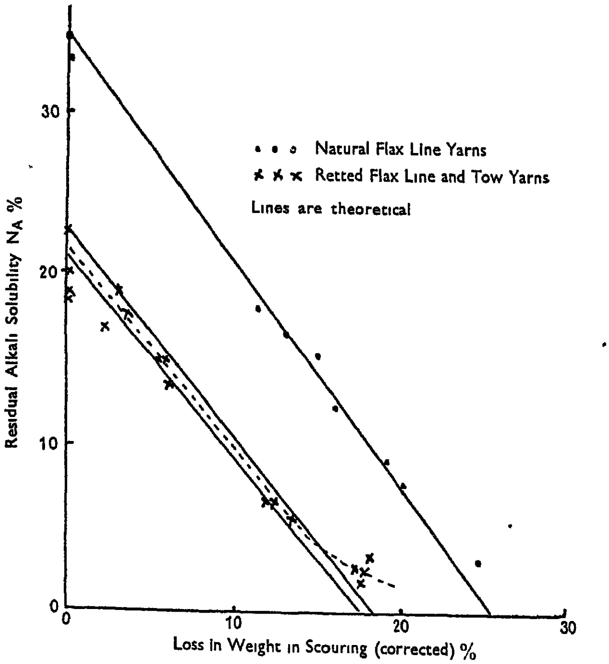

Fig 2

Loss in weight in scouring and residual alkali solubility (5% soda ash) %(N_A)

Now let the flax be scoured with a loss in weight of W per cent., (both original and boiled weights being on the oven dry basis), such that residual total soluble matter, on the boiled oven dry weight, is S per cent, i e $(100-S)$ parts insoluble matter are now associated with S parts soluble matter In the original yarn however, $(100-S_0)$ parts insoluble matter were associated with S_0 parts soluble matter $(100-S_0)$ parts insoluble matter are associated in the boiled yarns with $\frac{(100-S_0)}{(100-S)}S$ parts soluble matter whence weight loss,

$$W=S_0-\frac{(100-S_0)}{(100-S)}S \quad \text{. . . . . .} \quad 1$$

which may be rearranged thus—

$$W=\frac{100(S_0-S)}{(100-S)} \quad \text{. . . .} \quad 2$$

where S_0 is the solubility of the grey and S that of the boiled yarn This equation when plotted on graph paper does not, however, give the desired straight line relationship between loss in weight and residual solubility. A linear relationship may be obtained if we refer the residual solubility as a percentage of the insoluble content thus—

$$\text{Let } N_0=\frac{100\,S_0}{(100-S_0)} \text{ and } N=\frac{100\,S}{(100-S)} \quad 3$$

$$\text{Whence } S_0=\frac{100\,N_0}{(100+N_0)} \text{ and } S=\frac{100\,N}{(100+N)} \quad \text{. . .} \quad 4$$

Substitution of these values in equation (2) with rearrangement gives—

$$W=\frac{100\ (N_0-N)}{(100+N_0)} \quad \text{. . . . .} \quad 5$$

This equation is linear since N_0 is constant for any particular flax mix. When W is zero then $N=N_0$, when N is zero then $W=S_0$. Hence if our assumptions are tenable, points obtained by plotting N values against W values should be on a straight line joining the two points ($N=N_0$, $W=0$) and ($N=0$, $W=S_0$) whose slope is given by $100/(100-S_0)$ Hence, where the grey unboiled material is available, simple determination of S_0 and hence N_0 enables a boiling control line to be drawn Determination subsequently of S and N on boiled yarns should enable reasonably accurate wastage figures to be quoted This should obviate the present inaccuracies of bulk weighing of boiled yarn which may be overdamp or overdry and which is rarely given sufficient time or proper aeration in which to "condition" adequately The variation in alkali solubility relations from one flax mix to another still precludes any accurate indication of the probable loss in weight that any scoured yarn has suffered, if a grey control is not available

The severity of the scouring in the testing technique has preferably to be chosen so that virtually no soluble matter remains after treatment. It is recognised that the limit of severity would be obtained by determination of the cellulose content, as for example by the Cross and Bevan method, but this would be tedious and unnecessary as a works control procedure. The total loss in weight obtained by boiling for 2½ hours in 5 per cent soda ash solution, as in the alkali solubility method is reasonably severe, but is considered not severe enough to cover those cases where yarns have been scoured in bulk in caustic soda solutions This appears to be confirmed by plotting values of N_A (i e total solubility using 5 per cent soda ash liquor) against scouring weight loss for the present set of yarns (Fig 2). Although the points for the natural flax line lie close to the theoretical line, the points for the retted flaxes shew some deflection at the higher scouring weight losses.

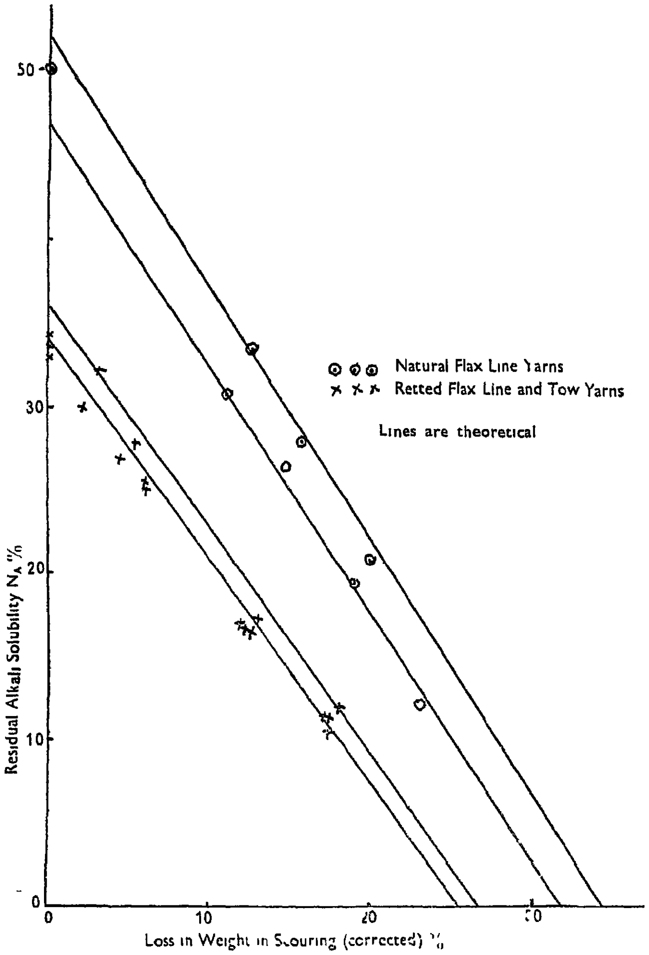

Fig 3

Loss in weight on scouring and residual alkali solubility (5% caustic soda) %(N)

Substitution of the 5 per cent soda ash liquor by 5 per cent caustic soda (Fig 3) appears to bring all points nearer to the theoretically expected straight lines and has been adopted for the present investigation. The adoption is, however, tentative pending a wider investigation as it may prove necessary to increase still further the severity of the testing scour The per cent losses in weight incurred during scouring have been corrected for the slight differences in moisture content between the grey and boiled yarns So corrected, percentage losses in weight on air dry weights are identical with those expressed on oven dry weights.

Fabric Tensile Strength

Examination of the figures in Table V shows, in the case of the retted flax line and tow fabrics, that as the alkali soluble content decreases, *i e* as the cellulose content increases, fabric tensile strength steadily increases in both the conditioned and saturated states Whilst this is also true for the natural flax line fabrics in the saturated state, the tensile strength in the conditioned state first decreases and then returns to its grey value at the highest cellulose content Taking grey and highest boiled values we have—

Table XII

		Grey Cond	Grey Sat	Sat / Cond	Boiled Cond	Boiled Sat	Sat / Cond	Boiled/Grey Cond	Boiled/Grey Sat
Retted Tow	Warp	10 7	15 1	1 41	12 3	19 1	1 57	1 15	1 26
	Weft	13 0	17 8	1 37	18·5	26 2	1 42	1 42	1 47
Retted Line	Warp	13 7	20 1	1 46	15·6	22 4	1 44	1 14	1·11
	Weft	18·7	20 1	1 07	24 8	34 8	1 41	1 33	1 73
Natural Line	Warp	13 6	15 7	1 15	13 8	20 0	1 44	1 00	1·27
	Weft	27·4	22 6	0 82	27 0	35 0	1 30	1 00	1 55

(Note Fabric strength is recorded here in lb /inch/oz)

On reference to Table VIII it will be noted that increase of grey fabric tensile strength on saturation roughly follows the increases shown by the grey yarns when wetted The sensitivity of the unboiled natural line weft to wetting, in its marked strength reduction, is again shown up in the fabric The fabrics prepared from boiled yarns also show a roughly similar order of increase when wetted as do the boiled yarns

It will also be observed by reference to Table VII that the increase of fabric strength, as yarns are progressively scoured, is much greater in both the conditioned and saturated states than the increases shown in actual yarn strengths Figure 4 shows yarn quality numbers (means of warps and wefts at 36 in and also 1 in) plotted against fabric tensile strengths (means of warps and wefts expressed in lb / inch / oz) It is concluded that the points for all three fabrics in both the conditioned and saturated states lie closely about two straight lines which pass through the origin Table XIII shows values for the ratio of the mean fabric tensile strength (in lb / inch / oz) to the mean yarn quality numbers (lb / lb)—

Table XIII

Fabric	36″ Quality Number Conditioned	36″ Quality Number Saturated	1″ Quality Number Conditioned	1″ Quality Number Saturated
Retted Tow				
Unboiled	13 3	13 9	—	—
15% A S	13 4	13 0	8 6	9 0
10% A S	12 2	13 1	8 5	8 6
5% A S	11 7	13 6	8 0	10 0
2% A S	12 2	12 7	7 8	9 1
Retted Line				
Unboiled	11 2	12 1	—	—
15% A S	12 6	13 2	9 0	10 8
10% A S	11 3	12 5	8 4	9 5
5% A S	10 7	12 0	8 6	9 5
2% A S	11 3	11 7	8 2	9 2
Natural Line				
Unboiled	14 8	14·2	—	—
15% A S	14 1	12 4	9 2	9 0
10% A S	11 1	12 9	7 8	10 0
5% A S	11 9	11·9	9 3	10 0
2% A S.	12 1	11 8	8 9	8 6
Mean	12 3	12 7	8 5	9 4
Mean	12 5±0 19		9 0±0 15	

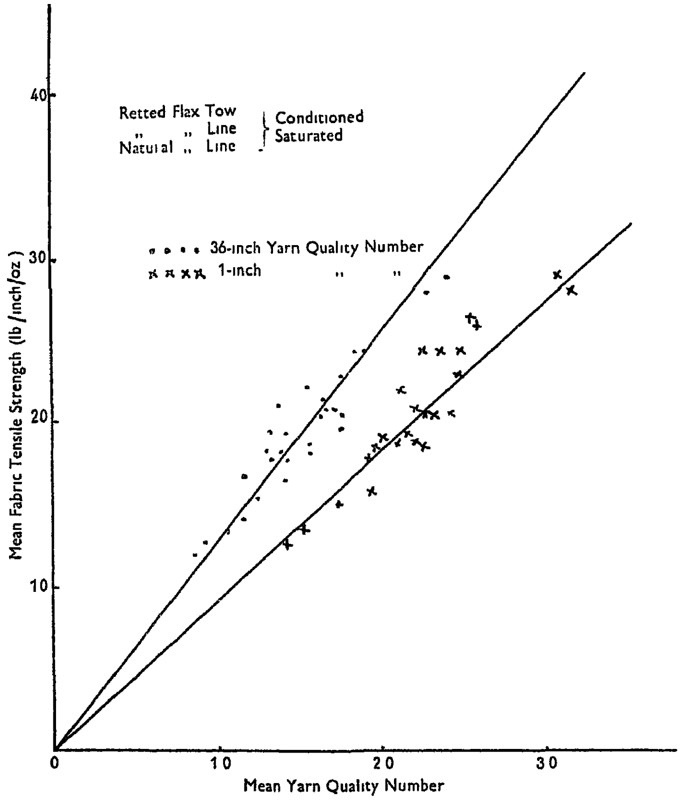

Fig 4

Mean fabric tensile strength and mean yarn quality number

It is concluded from these figures that an apparently simple relation exists between yarn and fabric tensile strength, at least within the type and range of fabric, yarn and fibre at present studied

Figure 5 shows residual caustic soda solubility factors or *N* values plotted against mean fabric conditioned tensile strength The retted tow values lie close to one straight line, and the retted line values close to another roughly parallel straight line The natural line values are erratic, but are situated near to the retted line group Figure 6 shows similar values plotted for saturated fabrics The retted tow points lie closely about one straight line, and both the retted and natural line fabrics about another, roughly parallel, straight line. It is suggested that this simple type relation between chemical purity and fabric tensile strength should be of some value in the design and construction of heavy fabrics

Fabric Tongue-Tear Strength

In the conditioned state the retted line fabrics are, on the average, of the highest tear strength, and are followed closely by the natural line fabrics The retted tow fabrics are the weakest On the average, saturation increases the tear strength of all fabrics, natural line by 42 per cent , retted tow by 32 per cent and retted line by 16 per cent Although the figures are somewhat erratic, a tendency exists in all the fabrics for increase in tear strength on saturation to become greater as the chemical purity of the fabric increases Figure 7 shows mean fabric tongue-tear strength plotted against *N* values.

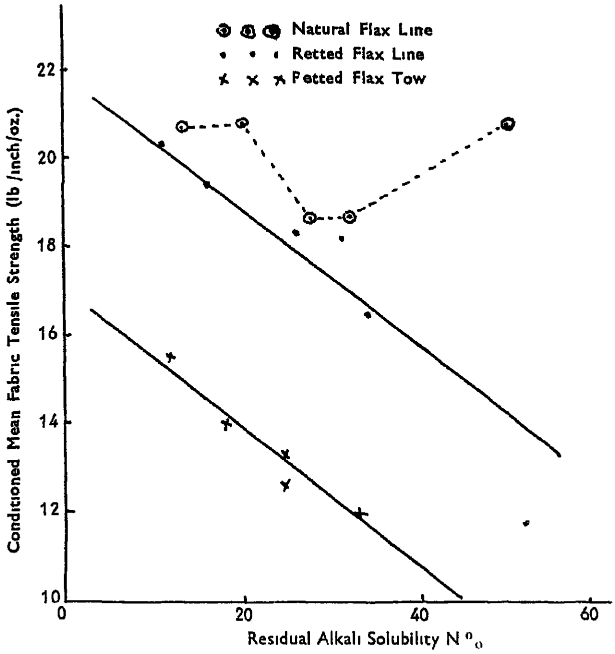

Fig 5

Conditioned mean fabric tensile strength and chemical purity —N%

In the conditioned state, retted tow fabrics appear virtually unaffected by the degree of scouring; retted line fabrics increase distinctly whilst natural line fabrics tend to fall in tear strength as chemical purity improves Upon saturation all fabrics tend to increase in tear strength as the content of residual soluble matter decreases The ratio of mean fabric tongue—tear strength (lb) to mean fabric tensile strength (lb./inch) appears reasonably constant over each range studied—

Fibre	Ratio of Mean Tongue-Tear Strength (lb) to Mean Tensile Strength (lb /inch)	
	Conditioned	Saturated
Retted Tow	0 36	0 33
Retted Line	0 38	0 32
Natural Line	0 32	0 37
Mean	0 35	0 34

If the mean yarn quality numbers are plotted against mean fabric tear strengths a scatter of points about straight lines is obtained The spread of points is not, however, close enough to warrant drawing any conclusion beyond observing the expected tendency for tongue-tear strength to increase as yarn quality number increases.

Summary

The main conclusions drawn from this work are summarized as follows—

(1) For any one flax fibre mix, as grey yarn grist is increased, quality number or intrinsic yarn strength also tends to increase

(2) Alkaline scouring of heavy dry spun retted flax tow yarns tends slightly to increase conditioned yarn tensile strength (as distinct from quality number or intrinsic strength). Retted flax line yarns appear to be unaffected whilst natural flax line yarns lose markedly in strength The severity of scouring does not appear to have any effect In the saturated state, however, alkaline scouring appears to increase the tensile strength, of all three types, by roughly the same amount (9 per cent).

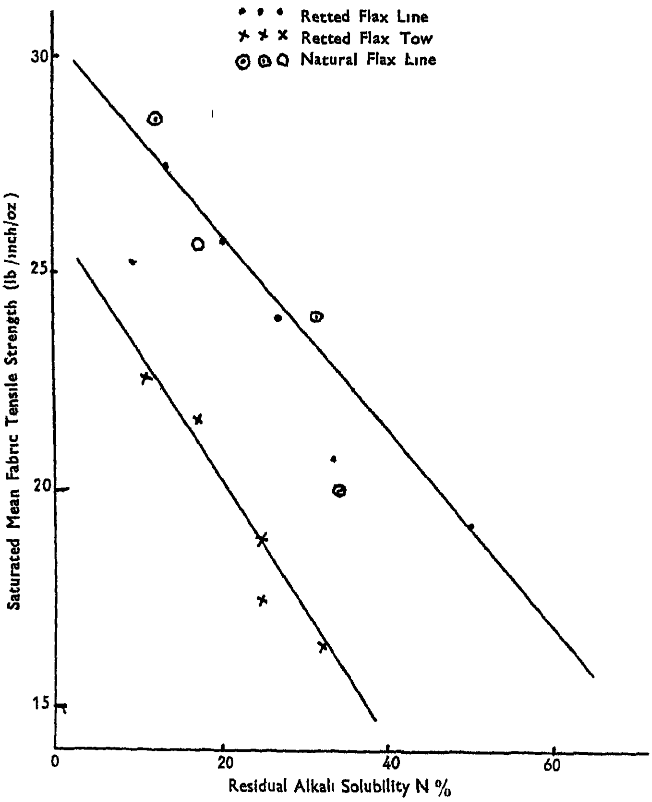

Fig. 6

Saturated mean fabric tensile strength and chemical purity —N%

(3) In the unboiled conditioned state, the line yarns are stronger than the tows, with natural line wefts outstandingly strong at an average quality number of 1·78 lb /lb. Upon saturation with water, however, whereas the retted tow yarns gain roughly 33 per cent. in strength in both warp and weft, retted line yarns gain only 20 per cent. in the warps and 9 per cent in the wefts Natural line warps gain only 5 per cent whilst natural line wefts lose 12 per cent in intrinsic strength, when wetted Scouring increases conditioned yarn intrinsic strength in all cases except for natural line wefts, which slightly decrease In the saturated state scouring increases yarn quality numbers in all cases

(4) The higher the content of matter insoluble in alkali at constant yarn grist, *i e* the greater chemical purity, the greater is the yarn intrinsic strength and the greater the increase in strength upon saturation with water.

(5) Natural or unretted flax line warps in this work are more irregular in

strength than the other yarns examined, due, it is suggested, to undergristing. Both scouring and saturation tend slightly to decrease the yarn strength irregularity.

(6) The effective increase in yarn tensile strength upon reduction of test length appears to vary with the type of fibre and to be slightly greater in the conditioned state than when saturated.

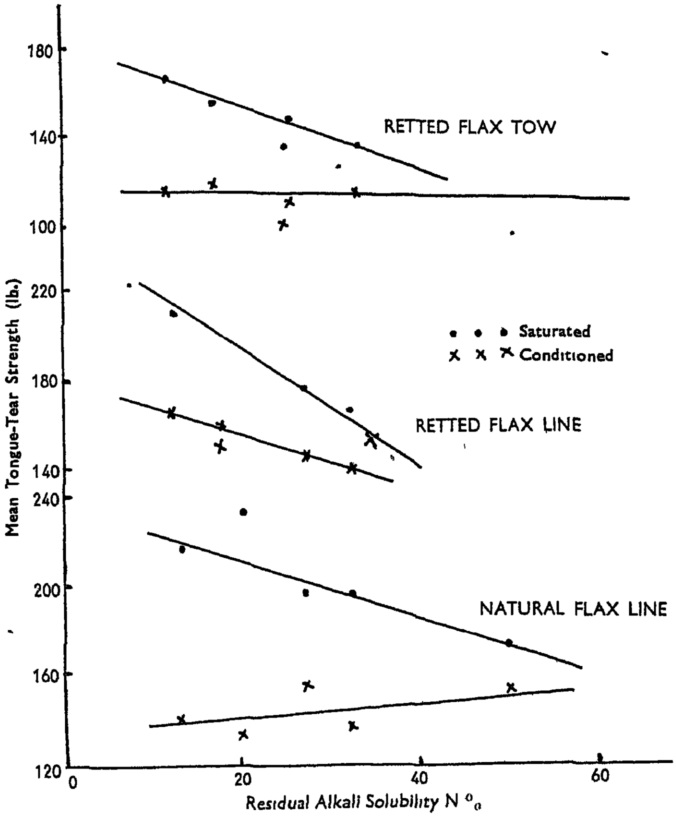

Fig. 7

Mean fabric tongue-tear strength and chemical purity —N%.

(7) Single fibre (i.e. single ultimate bundle) tensile strength appears to be greater for retted than for unretted fibre and to be higher for line than for tow. Evidence has been obtained that fibre strength is reduced slightly both by scouring and saturation, whilst elongation at break tends to increase slightly, at the same time.

(8) Yarn twist appears to increase definitely (7-8 per cent.) upon scouring of retted flax tow and natural flax line yarns. A smaller increase (3 per cent.) has been found for retted flax line yarns.

(9) The mathematical relation between loss of weight in scouring and residual solubility in further "complete" test scouring has been shown to be linear. Residual solubilities, termed *N* values, determined by the use, tentatively adopted, of boiling 5 per cent. caustic soda solution have been shown to fit closely to the theoretically expected straight lines, when plotted against weight losses.

(10) As the severity of scouring is increased, the average fabric tensile strength, in both the conditioned and saturated states, of retted flax tow and retted flax line fabrics, also increases In all cases the tensile strength of these fabrics increases upon saturation and the increase becomes larger as the severity of scouring is increased. Natural or unretted flax line fabrics show anomalous results as might be expected from the yarn properties. In the conditioned state, the average fabric tensile strength tends to fall as the natural flax yarns are boiled, but rises back to the grey values at the highest degree of chemical purity The tensile strength of the unboiled natural flax fabric falls upon saturation, but all fabrics made from boiled natural flax yarns gain in strength when wetted with water

(11) An approximately linear relation appears to exist between mean fabric tensile strength and residual caustic solubility or *N* values, for all fabrics in the saturated state. The retted tow points lie on one straight line whilst the retted and natural line values appear to be coincident about another roughly parallel straight line Similar lines are obtained with conditioned strength values but here the abnormal values given by the natural line fabrics are clearly shown. Similarly deductions may be made between yarn strength and *N* values although the scatter of points is much greater.

(12) Mean fabric tensile strengths plotted against mean yarn quality numbers 36 inch and 1 inch, (average of warp and weft) for grey, boiled, conditioned and saturated values give two scatters of points which lie fairly closely about two straight lines which pass through the origin.

(13) Fabric tongue-tear strength appears to be insensitive to the degree of chemical purity in the case of the retted tow fabrics in the conditioned state. Retted line fabrics show a slight increase, whilst natural line fabrics show a slight decrease in tear strength under similar conditions When saturated, all fabrics increase in tear strength and also increase as chemical purity is improved With all the three types of fibre, conditioned or saturated, the mean fabric tongue-tear strength appears to be roughly one-third of the mean fabric tensile strength

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REFERENCES

[1] Elkin, *J Text Inst*, 1935, 26, P201
[2] Searle, *J Text Inst*, 1929, 20, T162
[3] Meredith, *J Text Inst*, 1945, 36, T128.

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FIBRE MATURITY OF COTTON DIFFERENTIAL DYEING TEST

The Editor, *Journal of the Textile Institute*

The following account, in a more detailed version, has recently appeared elsewhere [8] It is submitted here for the benefit of English readers who may not be acquainted with the interesting work of Goldthwait and his colleagues

A test for the detection of immature, thin-walled cotton, using a binary mixture of direct cotton dyes, has been reported by Goldthwait, Smith and Barnett [5] The test involves a dyeing technique in which normal thick-walled hairs assume a red, and thin-walled, a green colour It is simple to carry out and of obvious usefulness for the pre-identification of neppy cotton.

The present communication concerns the application of this technique to viscose rayon in the form of staple fibre. Goldthwait has suggested[4] that the red and green dyes chosen may have some specific affinity, respectively, for thick- and thin-walled cotton celluloses We have not studied this possibility for such cottons, and that may be so But, based upon previous studies of dye diffusion into many forms of regenerated cellulose—in particular, viscoses of varying filament dimensions—it seemed to us that two known factors could themselves provide a basis for the very useful observations of Goldthwait *et al* These factors are.—

(1) Direct dyes may diffuse into cellulose at very widely different speeds. In fact, Boulton's figures[1] for the actual dyes used by Goldthwait *et al* are:

	Time of half-dyeing
Diphenyl Fast Red 7BL (C I No 278)	0 88 minute
Chlorantine Fast Green BLL . ..	55 2 minutes

These times are a roughly comparable measure of diffusing rates of the two dyes into a given cellulosic fibre

To this factor might be added the corollary that dyes which diffuse relatively rapidly also wash off into water relatively readily. This is cogent to the cotton maturity test, which includes a hot-water stripping after dyeing.

(2) If a thick fibre and a thin fibre are dyed together:

(*a*) The finer filament will dye the more rapidly in the initial stages on account of the greater surface per unit weight offered to the dye bath

Elements of fine-structure such as degree of orientation and closeness of intramicellar packing have a great influence on dye diffusion,[2,6,7] and this initial difference may be offset in the over-all dyeing process by differences in ease of penetration.

(*b*) In spite of any differences in dye-absorption rate, it will always happen that, when the two fibres have absorbed equal weights of dye per unit weight of fibre, the coarse fibre will appear the darker.[3]

With these factors in mind, we have taken the suggestion made by Goldthwait that the test might be tried on viscose rayon, and have used fibres of known coarse and fine deniers in place of thick- and thin-walled cotton.

Results and Discussions

(1) Influence of fibre thickness

Staple fibres, made up from Courtaulds bright "Fibro" 1·5-denier and 50-denier were dyed, in equal weights, exactly as in the test [5]

The results showed the fine 1·5-denier to be dyed green, and the coarse 50-denier to be dyed red. Dyeings on a range of fibres of increasing denier between 1·5 and 50 showed that the shade increased in redness with increasing denier up to the flat red given by the 50-denier "Fibro" (the range used was 1·5, 4·5, 8, 18, and 50 denier).

When examined before the washing in boiling water, all deniers had absorbed some red dye, the green shade on the finest denier developed only as this portion of red dye was washed out. Thus, fine-and coarse-denier "Fibro" behave, qualitatively, precisely as thin- and thick-walled cottons do. Mounted swatches of comparative dyeings have precisely the same appearance as the coloured photographs in the paper of Goldthwait *et al.*

The range of fibres was now dyed, in two separate sets, with the single dyes, using 1·20 per cent. Diphenyl Fast Red 7BL and 2·8 per cent. Chlorantine Fast Green BLL under the standard conditions.

In the case of the red, all deniers absorbed dye strongly, but depth of dyeing increased sharply with increasing denier. On applying the standard 30 seconds' boiling wash, all the fibres lost an appreciable proportion of dye. In the case of the green dye, all fibres were more nearly equal in depth, they lost very little dye in the 30 seconds' boiling wash.

A rational explanation of these results is as follows:—

Of any two dyed fibres of like composition but different thickness, the colour of the finer filament will always appear lighter in depth than the thicker for the same weight of dye per unit weight of fibre. This is a straightforward optical effect,[3] dependent on the fact that any beam of light entering the fibre and returning to the eye by reflection from inner surfaces has to traverse a shorter mean path in a thin than in a coarse filament. The depth of intensity of colour apparent to the eye is related directly to the mean path length.

This can be algebraically expressed in terms of amount of dye required to give equivalent depth:

Let C_F and C_C be the amount of dye found to give equivalent optical depth on fine and coarse fibres, respectively, and D_F and D_C be the mean diameters of these fibres. Then

$$\frac{C_F}{C_C} = \frac{D_C}{D_F}$$

Denier is proportional to diameter squared and

$$\frac{C_F}{C_C} = \sqrt{\frac{\text{coarse denier}}{\text{fine denier}}}$$

In our case,

$$\frac{C_F}{C_C} = \sqrt{\frac{50}{1\cdot5}} = 5\cdot8$$

To appear equal, the 1·5-denier fibre would need to have 5·8 times as much dye on as the 50-denier. Now with the rapidly diffusing red dye, the dyeings after 45 minutes' total dyeing time were approximately equal in dye content. The natural result of this is that the coarse fibre appeared about six times as intensely coloured as the fine.

Furthermore, in the boiling wash test there is more red dye washed off the fine than off the coarse filament, because there is much more surface per unit weight—that is, a very much larger water-cellulose interface. The areas of these surfaces stand in the relation of the fibre radii—that is, 5·75 to 33, which means nearly six times more interfacial area on the fine than on the coarse fibre.

The observable, and inevitable, result of all this is that the thin fibre comes out of the test with enough red dye to give a pale pink and the thick fibre is full red.

Now the dyeings with Chlorantine Fast Green BLL had shown that, in fact, there was little difference in depth between the fine and coarse fibres. We have said that, in theory and by observation, the coarse red dyeing was about six times as intense as that on the fine fibre with the same dye. This should be true also of the green dyeings, if, and only if, Chlorantine Fast Green BLL were at about the same concentration on each dyeing. But, unlike the red, which has reached equilibrium inside the 45 minutes of total dyeing, this green dye requires many hours to do so, and at 45 minutes the material is only in the initial stages of dye absorption. The actual results, using the test conditions, but progressively extending the dyeing time up to 3 hours, were as follows.

Time of dyeing minutes	15	30	45	60	120	210	360
	Percentage dyebath exhaustion						
Denier 1·5	0·7	3·3	10·8	13·5	18·1	22·2	23·1
Denier 50	0·0	2·3	3·7	7·7	11·6	15·3	31·4

We see from this that in the early stages 1·5-denier "Fibro" is dyeing more rapidly than 50-denier. This is commonly observed in dyeing mixed deniers, it is in the early stages that the fibre surface factor has the greatest influence. At the end of the dye test period, the fine fibre has more green dye than the coarse. It has not, however, the six times' excess that it should have to provide equality in appearance. But the fibres, at this stage, are not dyed throughout their thickness with the slowly diffusing green dye and the strict optical relation does not hold. As stated, the two 45-minute dyeings, containing 3·7 and 10·8 per cent. available dye, respectively, were almost equally intense to the eye. This relationship is not affected by the boiling-water strip, as none of the slowly diffusing green dye is removed from either fibre.

The net result of the differential dyeing rates of the two dyes, the differential optical appearance of the two dyed fibres, and the influence of fibre surface on both rate of dyeing and ease of stripping is to give, under the conditions of test, a fine filament which looks green and a coarse one which appears flat red, and this is what Goldthwait *et al.* have observed for their thin- and thick-walled cotton celluloses.

REFERENCES

[1] Boulton, J., *Soc. Dyers and Colourists*, 1944, **60**, 5.
[2] Boulton and Wardle, *J. Soc. Dyers and Colourists*, 1946, **63**, 8.
[3] Fothergill, *J. Soc. Dyers and Colourists*, 1944, **60**, 93.
[4] Goldthwait, *Private communication*.
[5] Goldthwait, Smith, and Barnett, *Textile World*, 1947, **97** (No. 7), 105.
[6] Preston and Kapadia, in "Symposium on Recent Advances in Theory and Practice of Dyeing," *Society of Dyers and Colourists*, 1947, p. 70.
[7] Rose, *J. Soc. Dyers and Colourists*, 1945, **61**, 113.
[8] Boulton and Armfield, *Textile Research Journal*, 1949, **21**, 212.

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Goldthwait, Smith and Barnett[1] have described a technique for differentiating between thick- and thin-walled cotton fibres by dyeing the cotton with specially selected green and red direct colours. Immature cotton is said to dye green and mature cotton pink We have dyed samples of raw cotton and drawframe sliver using their technique and have prepared fibre arrays from them using the comb sorter method described by Clegg[2] and black velvet pads

We found that all diagrams had greenish fringes and a deep pink centre band, which grew less intense near the short fibre end of the diagram. Examination with a magnifying glass suggested that the middle of most long fibres was pink and that they had greenish ends Some of the short fibres also appeared to have pink middle portions and green ends, whilst other short fibres appeared to be mainly green or mainly pink

To confirm our findings we selected from a sample of dyed drawframe sliver tufts of fibres which appeared to be pink and tufts which appeared to be green, and which, according to Goldthwait, Smith and Barnett, ought to have consisted of thick- and thin-walled fibres, respectively Fibre stapling diagrams made from these selected tufts again had green fringes and a pink central band, the main difference being that the intensity of the central band and the length of the fringes varied Cotton fibre immaturity count tests[3] and hair weight per centimetre tests[2,3] were also made on tufts selected from the drawframe sliver before dyeing and on selected tufts of dyed fibres, the following results being obtained –

	Undyed fibres (Random sample of 64 tufts)	Tufts of selected fibres	
		Pink Fibres	Green Fibres
Hair weight per cm $\times 10^{-8}$ gram	175	201	253
Immaturity count (normal %—dead %)	40 – 16	50 – 16	43 – 14

Our test results suggest that the results obtained from the differential dyeing technique are seriously affected by factors other than fibre maturity

REFERENCES

[1] C F Goldthwait, H. O Smith and M P Barnett, *Textile World*, 1947, **97**, No 7, 105.
[2] G G. Clegg, *J. Text. Inst*, 1932, **23**, T35
[3] E Lord, *J Text Inst.*, 1947, **38**, T84

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THE JOURNAL OF THE
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28—A MICROSCOPICAL EXAMINATION OF WORN TEXTILE ARTICLES

By Gladys G Clegg, M Sc.

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I. INTRODUCTION

A survey of the literature relating to the testing of fabrics in order to foretell serviceability shows that interest so far has been centred in the design and performance of the testing instruments rather than in the effect on the textile fibres of wear in service. This paper deals essentially with the microscopical examination of fibres from worn garments, the mechanism of their breakdown and their comparison with fibres from cloths which have been subjected to laboratory tests.

Resistance to what is commonly known as wear involves a number of properties and qualities of a garment and the factors involved in the breakdown and removal from service of the garment are numerous For instance, the majority of shirts fail in service owing to wear on the collars and cuffs, to splitting or tearing of the fabric, and sometimes to shrinkage, white overalls from a physical testing laboratory show wear on their edges, on the elbows, pockets, collars and other places, whereas those from a chemical laboratory

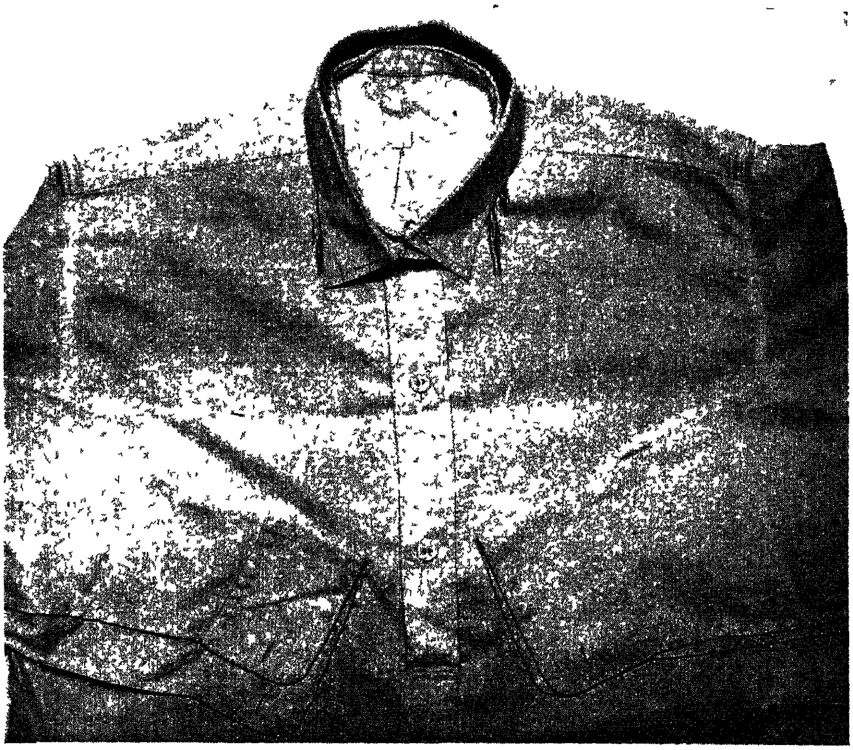


Fig 1 Photograph of worn shirt

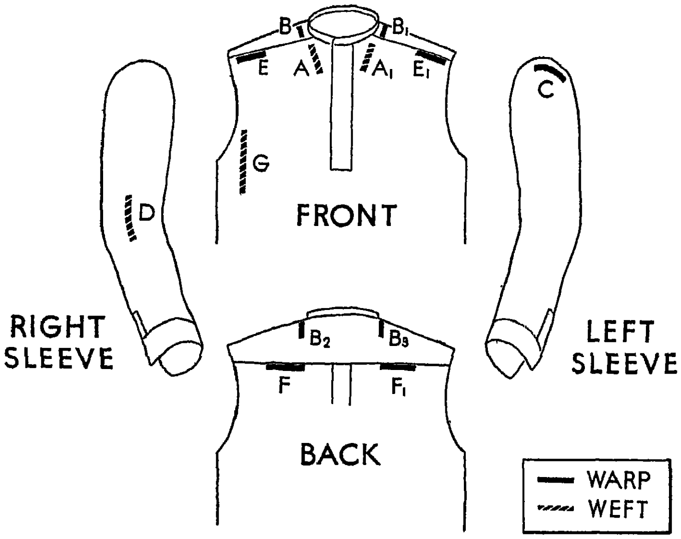


Fig 1 (*a*)
Diagram depicting breakdown of a poplin shirt.

become unwearable because of holes made by corrosive chemicals before there is any evidence of abrasive wear; coated raincoats fail because of cracking of the coating, umbrellas split down the creases made in folding, curtains show breakdown as a result of deterioration due to light tendering and velvet and corduroy garments are usually discarded for loss of pile. These are only a few examples of fabric breakdown, but they are sufficient to illustrate the difficulty of designing a composite wear test, and the necessity for testing the individual factors that contribute to the breakdown of the particular article under investigation

The lack of correlation between some of the results of laboratory tests and wear in service is well known and for some considerable time the necessity for more information on the mechanism of breakdown of the individual fibres has been realised This information is needed particularly for the design of cloth structures for specific purposes and for the design of machines to evaluate the suitability and serviceability of fabrics for these purposes It is essential to know

(*a*) What happens to the fibres during wear and breakdown of the fabric, and

(*b*) Whether a similar effect is produced on the fibres by the testing machines.

For these reasons a systematic examination has been made of fibres from worn textile articles and garments during and at the end of their useful lives.

The cotton garments and articles examined have comprised 70 shirts handed in as unserviceable, 95 overalls in course of wear, 50 overalls handed in as unserviceable, 68 white overalls and 113 khaki overalls made from experimental fabrics most of them still in use and subjected to regular examination. In addition, pyjamas, handkerchiefs, cushion covers, umbrellas, cotton frocks, brassieres, sheets, pillow slips, pile fabrics used for tyre covers, coated leggings, shoelaces, kitchen blinds, and fire hose pipes have been included in the examination

II. METHOD OF EXAMINATION

Each garment was thoroughly inspected and a record was made of the structure of the cloth, the position and type of breakdown, and how far and in what manner the warp and weft respectively contributed to this breakdown Microscopical examination was made of the fibres from the worn and torn portions. The fluidity[1] of the material was determined from the worn parts of the garment and when possible from those parts of the garment which had suffered least wear and tear

The Congo Red staining method[2,3] was used for the microscopical examination of the fibres, the mounts being examined with a 10× eyepiece, a ⅔ in objective, and daylight illumination

Photographs were taken of the early preparations but later it was decided that hand-coloured drawings made directly from the preparations gave a more adequate picture of the treated fibres. Photographs have been included when considered necessary

III. BREAKDOWN OF COTTON FABRICS IN USE

Examinations of all the garments has shown certain well-defined factors which contribute to breakdown but which function in varying degrees All the factors are involved in the breakdown of a poplin shirt worn with a starched collar, this breakdown is described in detail, and subsequently it will be shown to what degree each factor functions in the breakdown of the rest of the garments and articles.

(A) EXAMINATION OF A WORN SHIRT

The shirt chosen (Shirt 14) as typical is made from a mercerised end and end poplin, brown and white with a white weft. The warp has 149 ends of 86s/2 count, and the weft has 76 picks of 110s/2 count. The collar is stiff, made from a fine fabric, bleached and starched, with the warp of 102 ends, 41s count, and the weft 98 ends, 45s count. The collar has a coarser backing cloth and an interlining.

(i) Location of Wear and Tear

The general breakdown of this particular shirt is depicted in Fig. 1 (*a*) and comprises.—

(*a*) Wear on the edges of the collar and cuffs.
(*b*) Splits at front A-A1 (weft damaged.)
(*c*) Small holes on shoulder B, B1, B2 and B3.
(*d*) Split at top of left sleeve, C, breakdown of warp, and at the elbow of the right sleeve, D, breakdown of weft.
(*e*) Breaks at front and back, near saddle E and E1, F and F1.

In addition to the breakdown, the fabric, particularly at the front near the armholes, at the back over the shoulder blades, and at the top of the sleeves is very weak both in warp and weft direction.

(ii) Fluidity Determination

The fluidity in cuprammonium[1] was determined on the fabric from the worn portion at the top of the sleeve and on the comparatively strong fabric from the tail The figures of 14·9 and 14 7 obtained indicate that chemical deterioration as shown by the fluidity figures[4] only accounts for a drop in strength of approximately 12 per cent and that the fluidity is the same at those parts of the garment which have suffered both the greatest and least loss in strength

(iii) Mechanical Breakdown

(a) Wear of Collar

The collar shows wear along the folds and examination under the microscope reveals damage to both the warp and weft crowns, the appearance indicating the removal of a varying amount of the crown by abrasion The damaged fibres, firmly embedded in the starch, on treatment by the Congo Red staining method show the appearance depicted in Fig 2. The fibre ends appear brush-like owing to the disappearance of the cuticle and the loosening and breakdown of the fibrillar structure. This is an appearance consistent with fibre abrasion and the conclusion is drawn that the breakdown of the yarns in the collar fabric is due to abrasion of the individual fibres

(b) Breakdown of the Fabric of the Shirt

A poplin is a plain cloth woven from moderately fine two-fold yarns with twice as many ends as picks. The result of this structural balance is a low crimp in the weft and a high crimp in the warp, the warp being prominent on the surface of the cloth, which is thus virtually warp faced Although a cloth of this type might be expected to show most of the wear on the warp only, the shirt not only shows damage to the warp crowns in several places, but tearing of both warp and weft, and a general fabric weakness in both the warp and weft directions.

Fluidity figures have shown that chemical deterioration is responsible for only a small proportion of this general weakness Some other evidence must be sought to explain why some parts of the fabric, which show no obvious signs of wear, are easily torn in either direction when only a very small tension is applied.

Staple diagrams[5] of the fibres pulled down from the warp and weft yarns have been made and provide some explanation of this weakness. The fibres for the diagram of the warp yarn were taken from yarns at the front near the shoulder, but those for the weft were taken separately from three parts of the shirt,

(*a*) At the front near the neck opening where weakness is most marked.
(*b*) From the portion of the back over the shoulder blade.
(*c*) From the tail, which is comparatively strong.

The result of these stapling tests are given in Table I together with the figures for the weft of an unused poplin of approximately the same structure; figures for the wefts of two other shirts (Shirts 29 and 16) are also included.

Table I

		Effective length	% Short fibre	Mean length
Shirt 14 (Fig 3) Fluidity, 14 8	Warp (86s/2)	30/32″	69	14/32″
	Weft (110s/2) from			
	(*a*) Front near opening	19/32″	65	9/32″
	(*b*) Back near shoulder	31/32″	56	17/32″
	(*c*) Tail	35/32″	44	21/32″
Unused Poplin B.O C 3 (Fig 3) Fluidity 4 4	Weft (100s/2	42/32″	39	28/32″
Shirt 29 Fluidity (12 5)	Weft (110s/2) Front	35/32″	30	23/32″
Shirt 16 Fluidity (15)	Weft (60s/2)	32/32″	49	15/32″

The figures show

(1) A reduction in effective lengths ranging from 18 per cent. to 56 per cent with a corresponding increase in the amount of short fibre.

(2) A variation in the staple from different parts of the shirt which is correlated with the strength.

Fig 3 is a reproduction of the staple diagrams of the weft of Shirt 14 and of the unused poplin

Examination under the microscope of the weft yarns and fibres The weft yarns under the microscope give no evidence of abrasion but the number of protruding fibre ends is abnormal for a 110s/2 yarn. On examining the fibres after treatment by the Congo Red method a fair proportion have the appearance seen in Fig. 4. They display bright red transverse markings, cracks, and an obvious tendency to segment and break across these cracks. These markings range from faint red lines across the fibres to very obvious cracks. They are randomly distributed both along the fibres and from fibre to fibre and appear more numerous in the thick-walled rigid fibres. The markings occur along the whole length of some of the fibres at intervals of about 20μ; fibres in the same vicinity may be entirely devoid of markings.

In addition to the reduction in staple length there is a very definite weakening of the single fibres. The breaking loads, in grams, of centimetre- and of millimetre-lengths of the fibres from the weft yarns were determined with the results shown in Table II.

Table II

	Length	Breaking load in gms.
Shirt 26, Fluidity 12·5	1 cm	2 8
	1 mm	3 8
Unused poplin, Fluidity 4 4	1 cm.	6·3
	1 mm	8 4

These figures show a reduction in strength of more than half that of the fibres from the unused poplin The fact that the strength of millimetre lengths show proportionately the same reduction as the centimetre lengths indicates that the weakening occurs along the whole length of the fibre, which is consistent with the presence of the transverse markings and cracks.

Examination under the microscope of the warp yarns and fibres. Examination of the warp yarns from the cuffs and all portions of the shirt where the warp yarns are weak and in many places obviously worn shows the expected disappearance of the crowns. On treatment by the Congo Red method the appearance is very characteristic (Fig. 5). Numerous fibres protrude from the yarn, each showing similar cross markings to those seen in the weft fibres, and one fibre at the top of the crown gives evidence of damage, usually bruising, or gentle abrasion, occasionally accompanied by cross markings. Examination of the warp yarns from all parts of the garment shows the process of breakdown as depicted in Fig. 6. The top fibre in the crown is damaged and breaks, leaving two fibre ends standing. The process is repeated, the top fibres breaking down in succession until the yarn is finally severed. The broken fibre ends show an increasing number of cross markings and cracks, and pieces of the fibres break off.

This is the typical breakdown of the warp and occurs in all parts of the garment in varying degrees The damage to the fibre at the top of the crown varies in type and may show abrasion with fibrillation (Fig 7*a*), bruising, very gentle abrasion affecting the cuticle only (Fig. 7*b*), cross markings and transverse cracking (Fig 7*c*)

In concluding this description of the breakdown of a shirt it is perhaps useful to summarise the effects on the fibres and their significance in the general breakdown.

(1) The yarns and fibres in the collar held firmly in the starch are abraded and fibrillated (Fig 2).

(2) The weft protected by the warp cannot suffer abrasion but the fibres are bent, flexed, and subjected to extension and compression so that they crack transversely and break up along these cracks. This accounts for the weft-way weakness of the fabric and the tear at D (Fig. 1*a*) The splits at A and A1 are due to cracking of the weft along a crease which persistently forms in this position.

(3) The warp is vulnerable to abrasion but the fibres are on the whole free to move although single fibres may be held. The fibres in the crowns break down in succession but because these fibres are mobile they evade an intense abrasive action although they may be bruised, gently abraded or cracked transversely.

This type of breakdown in its early stages accounts for the general weakness of the fabric in the warp direction, and is responsible for the breakdown at C. More intense damage of this type is present at E, E1, F and F1 where the warp is damaged and disappears owing to rubbing by the braces, similar damage is present at B and B1, B2 and B3 caused by pressure and rubbing by the edge of the waistcoat The wear of the warp at these places is in accordance with the breakdown depicted in Figs. 5 and 6.

The factors, therefore, which have contributed to the breakdown of the shirt are

(1) Chemical deterioration

(2) Mechanical breakdown consisting of

  (*a*) Fibre abrasion of varying intensity.

  (*b*) Transverse cracking of the fibres.

(B) EXAMINATION OF GARMENTS AND OTHER ARTICLES

The examination of the rest of the garments and articles was carried out in a manner similar to that employed for the shirt The location of wear in garments and articles will be dealt with in a further Memoir In the present Memoir the results of the examination of the various garments are used solely to present the type of fibre breakdown which occurs.

With the exception of occasional biological attack (mildew, bacteria) the breakdown is found to be due to the three factors responsible for the breakdown of the shirt, namely, chemical deterioration, fibre abrasion, and transverse cracking of the fibres in varying proportion The results of the examination are dealt with under these headings.

(i) Chemical Deterioration

The fluidity figures for all the cotton garments and articles examined are given in Table III The trouser pocketings had been cleaned but not laundered, about one-third of the shirts and brassieres, corsets, and cushion covers had been home laundered, the rest of the shirts and all the overalls had been washed regularly at a commercial laundry.

Table III

Fluidity Figures for Cotton Garments at End of Useful Life

Trouser pocketing	5–7
Shirts (70)	10–20
Umbrella (sulphur blue)	13
Sheet (raised weft)	14
Wool-cotton mixture pyjamas (cotton)	14
Skiing gloves	14
Brassieres, corsets	15–19
Handkerchiefs	17–37
Sheets and pillow-slips	17–22
Shirley Institute experimental overalls after 4 years' wear	11–20
White overalls	24–34
Cushion covers	28
Pyjamas—satin striped poplin	30
Umbrella (aniline black)	35–36
Cotton canopy	40
Kitchen blind	41

These figures are remarkable in that they show how small a proportion of the weakness of shirts, sheets, pillow slips and overalls which have been laundered regularly, is due to chemical deterioration.[4] The fluidity figures for the shirts account for losses in strength of approximately 10-25 per cent., for the sheets and pillow slips 20-25 per cent The first set of white overalls examined, most of them of very poor quality and in a very worn and torn state when handed in, give chemical deterioration of 30-40 per cent., but the overalls made from experimental fabrics designed at the Shirley Institute and which have been in use for four years, with laundering on alternate weeks, show lower fluidity corresponding to strength losses of only 8-25 per cent.

The high fluidity figures for the aniline black umbrellas, cotton canopy (tendered by light and atmosphere), kitchen blind (tendered by gas fumes and light) are not unexpected and their retention in service in such a condition of chemical deterioration is explained by the absence of mechanical wear and tear suffered in use

(ii) Mechanical Breakdown

(*a*) *Fibre Abrasion.*

Breakdown due only to abrasion of the individual fibres has been found in a variety of articles, a list of which is given in Table IV, Col. A.

Table IV

Mechanical Breakdown of Cotton Garments and Articles

A Abrasion	B Transverse cracking	C Gentle abrasion and transverse cracking
Khaki dyed overalls and boiler suits (heavy work)	Handkerchiefs	Shirts
Starched cuffs and collars	Umbrellas	Pyjamas
Shoe laces	Weft of poplin shirts and pyjamas	Overalls
Pile tyre fabrics	Acetylated stripes	Cotton frocks
Coated leggings	Some pillow cases and cushion covers	Trouser pockets
Cycling and skiing gloves		Cotton linings
		Jacquard harness
		Sheets
		Pillow-slips

All these articles in Col A have one condition in common, the fibres are firmly held and therefore in a condition to be subjected to abrasive action

The khaki-dyed overalls and boiler suits have been used on heavy work in the Institute's engineering shops The abrasion occurs chiefly at the front where the fibres are held by tension or pressure as the fabric is pressed against the bench or some other hard surface.

Fibre abrasion occurs in coated leggings after the coating has cracked or peeled off and the fibres are exposed. These fibres are held by the coating just as the fibres in the starched collars and cuffs are held by the starch

The abrasion of the shoe laces which are used under tension occurs at the metal eyelet and is probably increased by the pressure of some road dust.

The palms of cycling and skiing gloves in Col A are held taut and the fibres in the pile tyre fabric are subjected to pressure and abraded by the rough surface of the road.

(*b*) *Transverse Cracking of the Fibres.*

In none of the articles in Table IV, Col. B, are the fibres held by tension, pressure, or filling and all are free to move. They are not vulnerable to abrasion but are subjected to bending, flexing, or compression and break up is due to transverse cracking.

The acetylated cotton fibres are sometimes more brittle than ordinary cotton fibres. Although the acetylated yarns are introduced as warp stripes in a poplin weave the usual breakdown of a poplin warp is not shown but the fibres break up like those of the poplin weft (Fig. 8).

(*c*) *Gentle Abrasion and Transverse Cracking*

The mechanical failure of the majority of textile articles (Table IV, Col. C) is similar to the breakdown of a poplin warp, and is caused by both abrasion and transverse cracking. Fibres held fairly firmly by the structure (fine sheets, pillow slips containing a hard filling such as flock), or by a light starching (white overalls, cotton frocks) will receive a fairly intense abrasion (Fig. 9). Fibres which are loose in the structure show abrasion of a gentler type which affects the cuticle only and may show when stained as a fringed red edge instead of a clean break along the cuticle spiral (Fig 10*a* and *b*), or the cuticle may be loosened, torn and partly or completely removed, giving the fibre a bruised appearance (Fig 10*c*) Bending and flexing of these fibres in addition to the abrasion, results in their breakdown (Figs. 10 and 11).

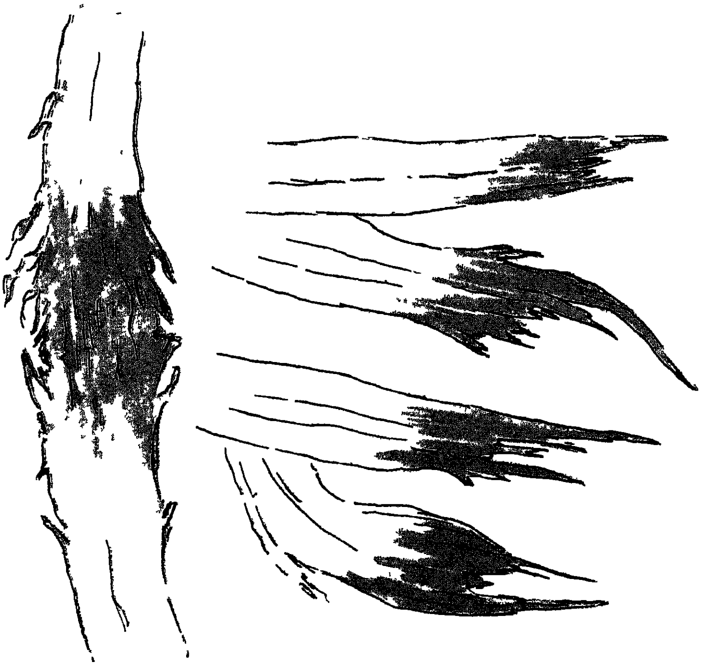
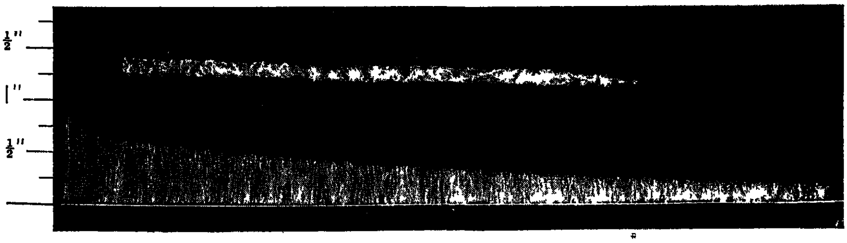
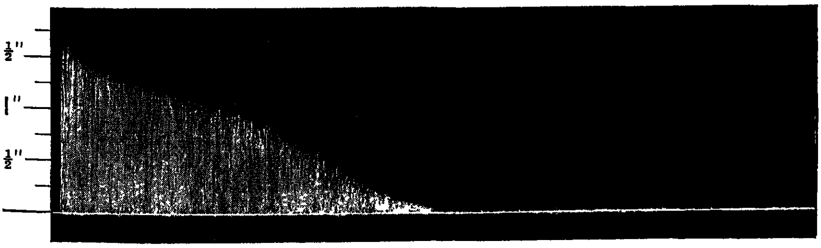


Fig 2

Fibres from fold of worn, stiff (starched) collar showing abrasion and fibrillation



Staple diagram of fibres from weft of shirt, 14-in front, near neck



Staple diagram of fibres from weft of unused poplin

Fig 3

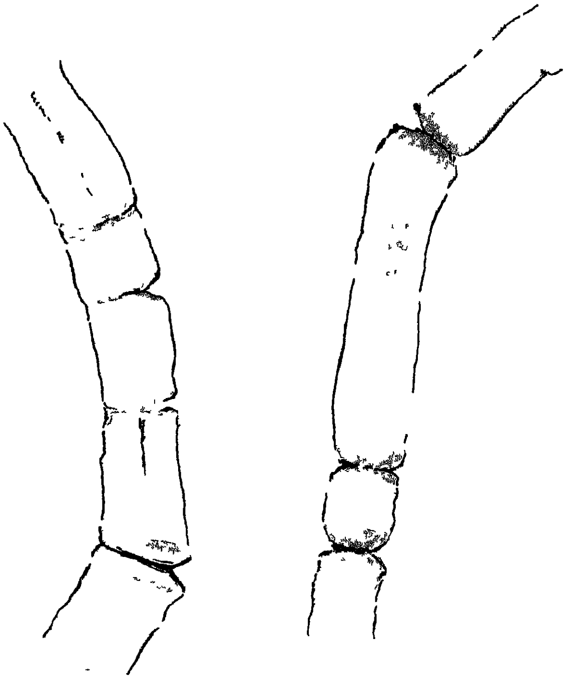


Fig 4
Fibre from the weft showing transverse markings and cracks

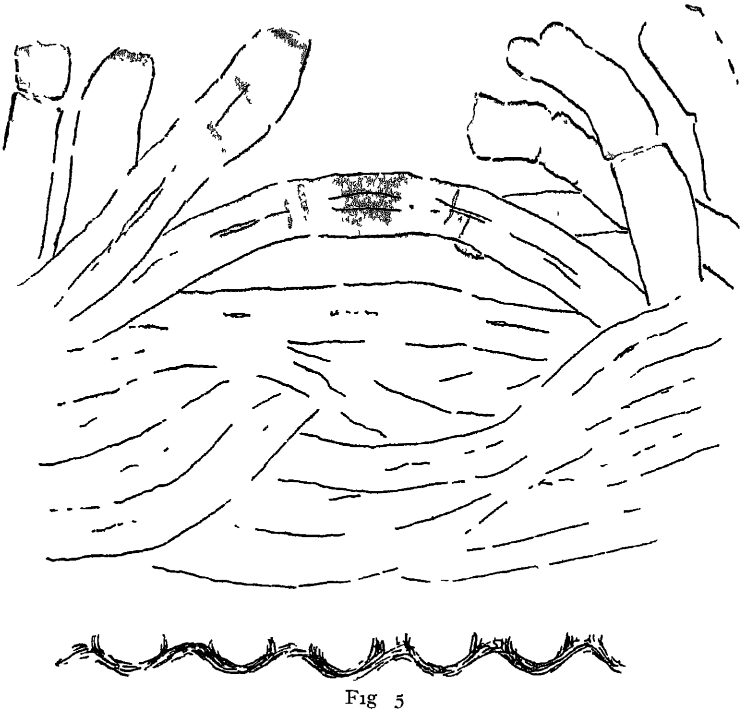


Fig 5
Damaged poplin warp crown showing bruised top fibre, and protruding fibres showing transverse markings and cracks

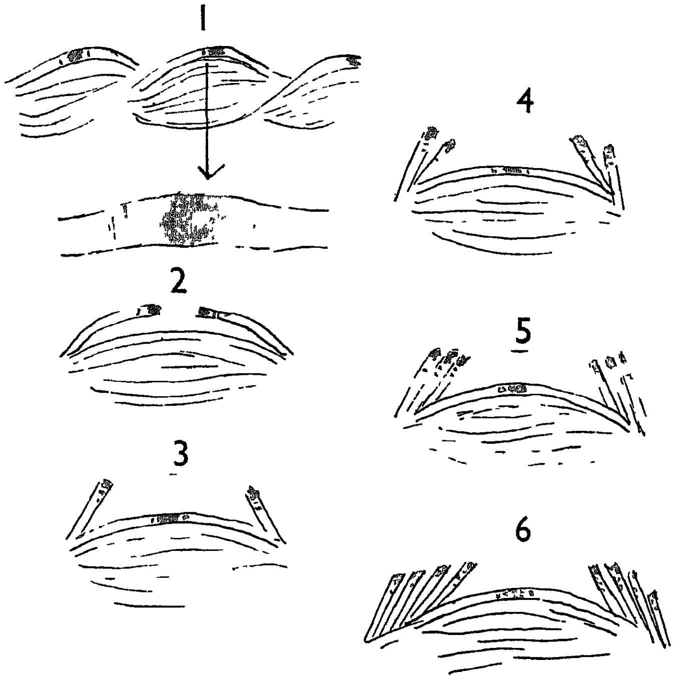


Fig 6

Diagram showing stages in the breakdown of a poplin warp

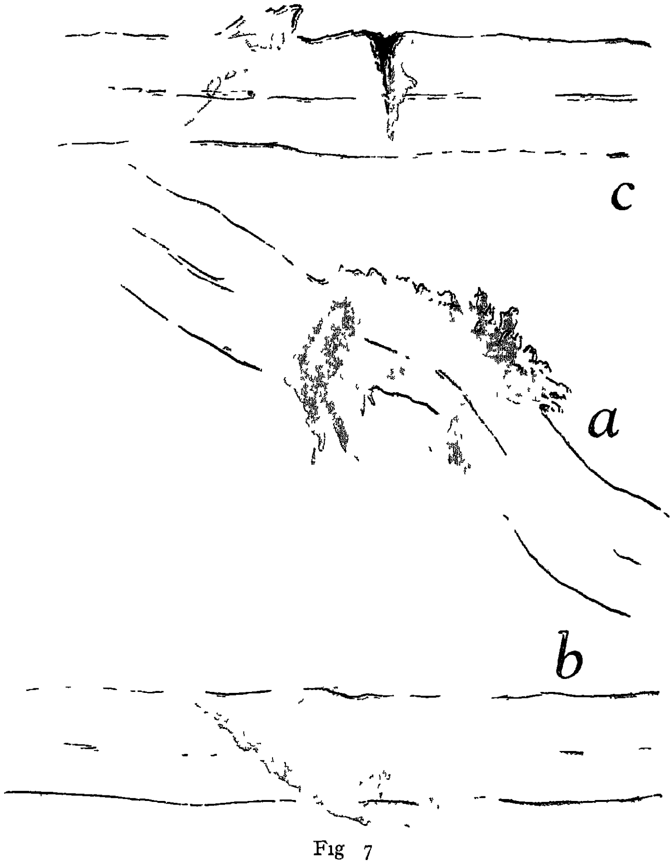


Fig 7

Types of damage seen in the topmost fibre in a damaged poplin crown, (*a*) Abrasion, (*b*) Cuticle abrasion and (*c*) Transverse cracking

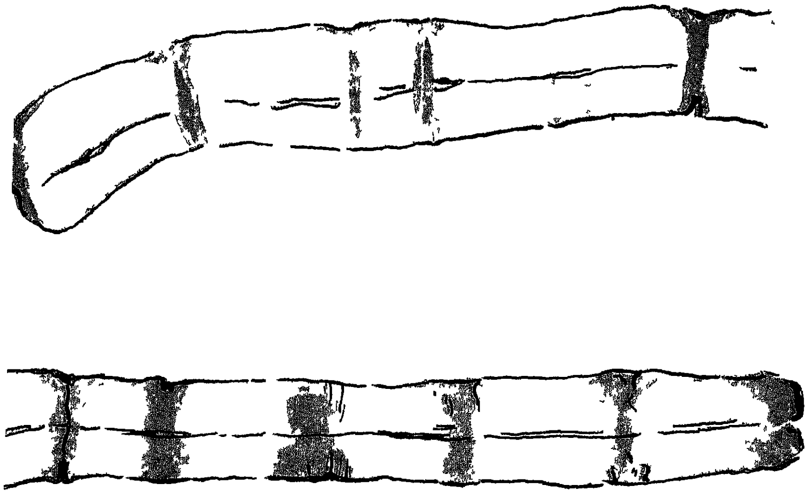


Fig 8
Fibres from acetylated stripes in a poplin shirt

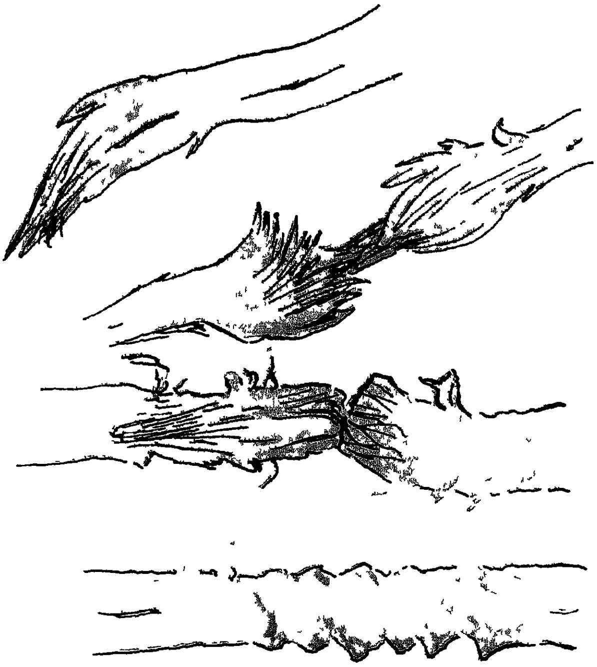


Fig 9
Fibres from the cuff of a starched overall cuff (4×2 twill) showing a fair amount of abrasion and fibrillation of fibres

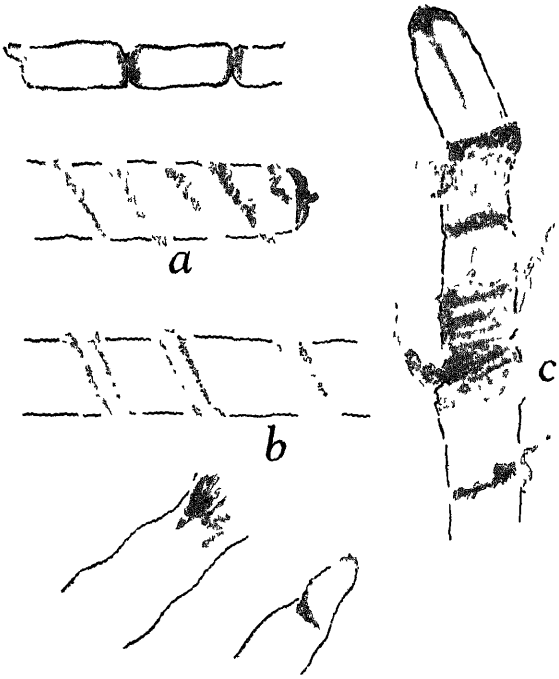


Fig 10
Fibres from the cuff of overall (2 × 1 twill) showing very gentle abrasion and transverse cracking of the fibres

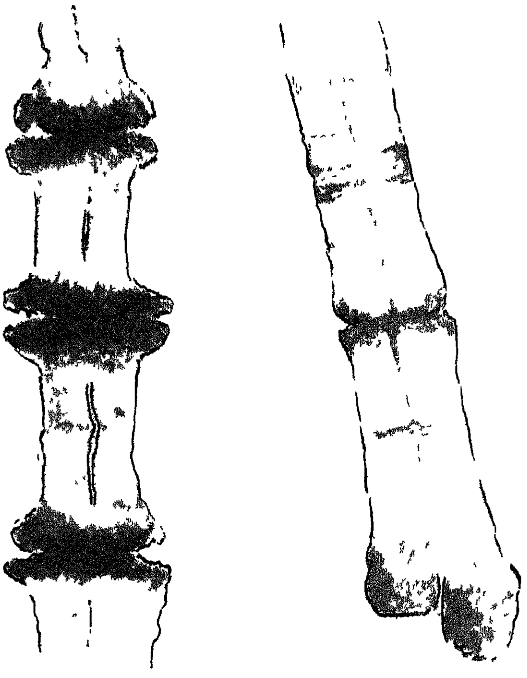


Fig 11
Fibres from weft of trouser pocketing showing gentle abrasion and transverse cracking.

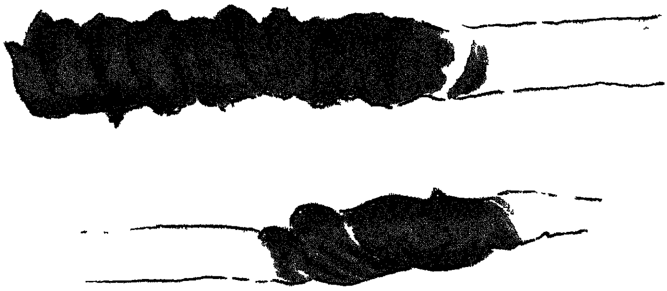


Fig 12
Fibres from binder of camel hair belting showing results of flexing, probably accompanied by bruising

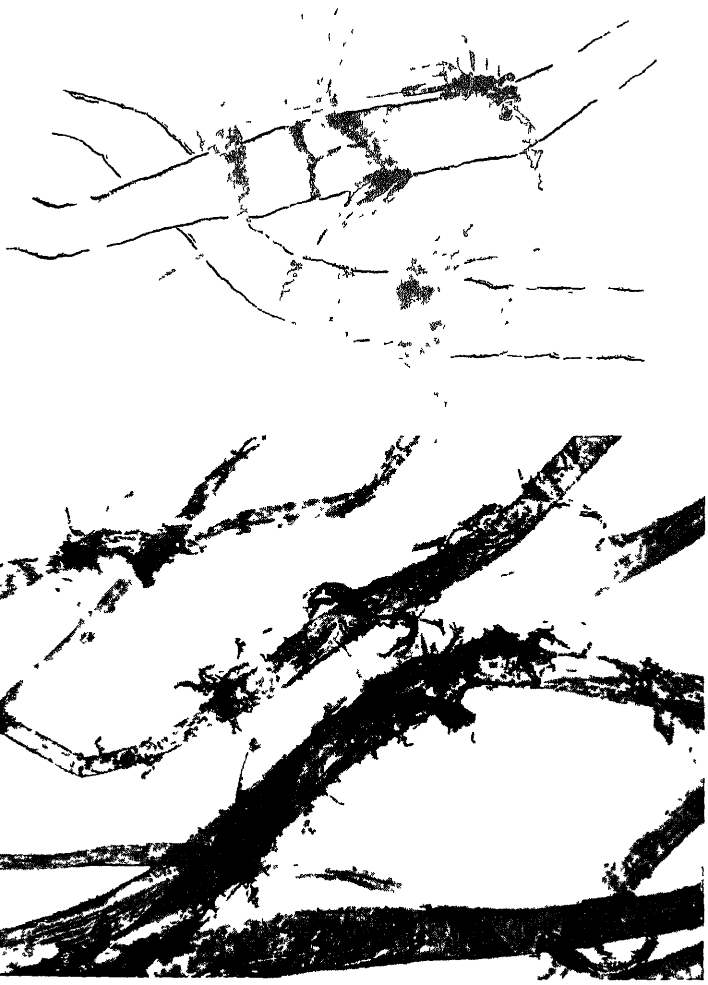


Fig 13
Fibres from linen damask table cloth showing abrasion

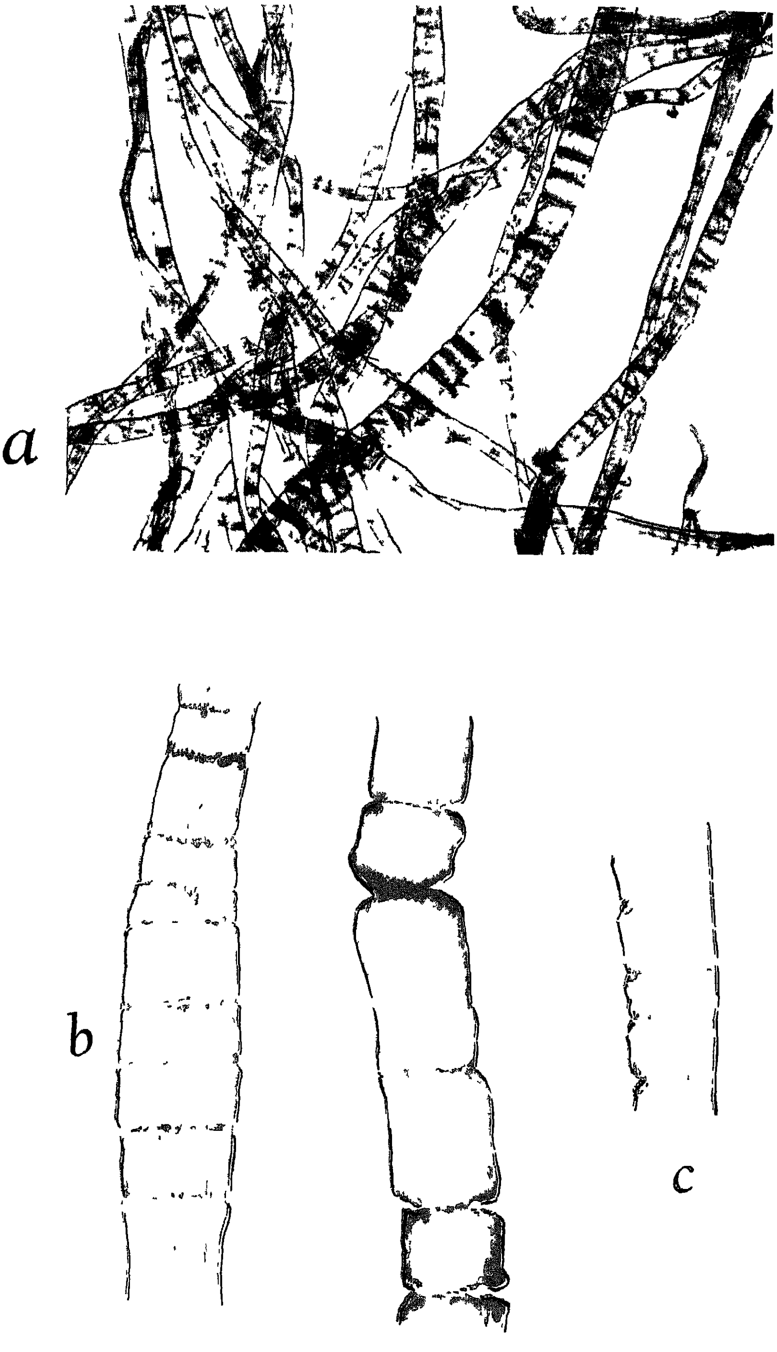


Fig 14
Fibre from worn linen pillow slip showing transverse markings and cracks

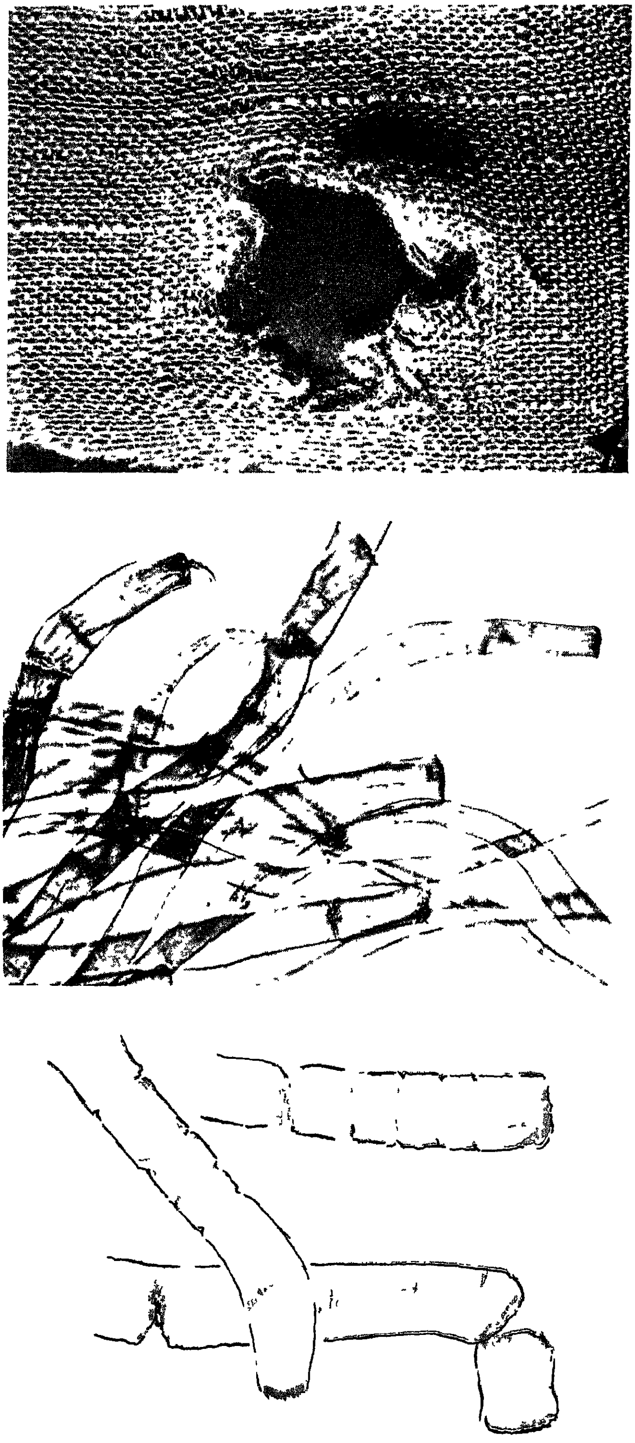


Fig 15
Hole from under-arm of linen frock and fibres from broken yarn ends

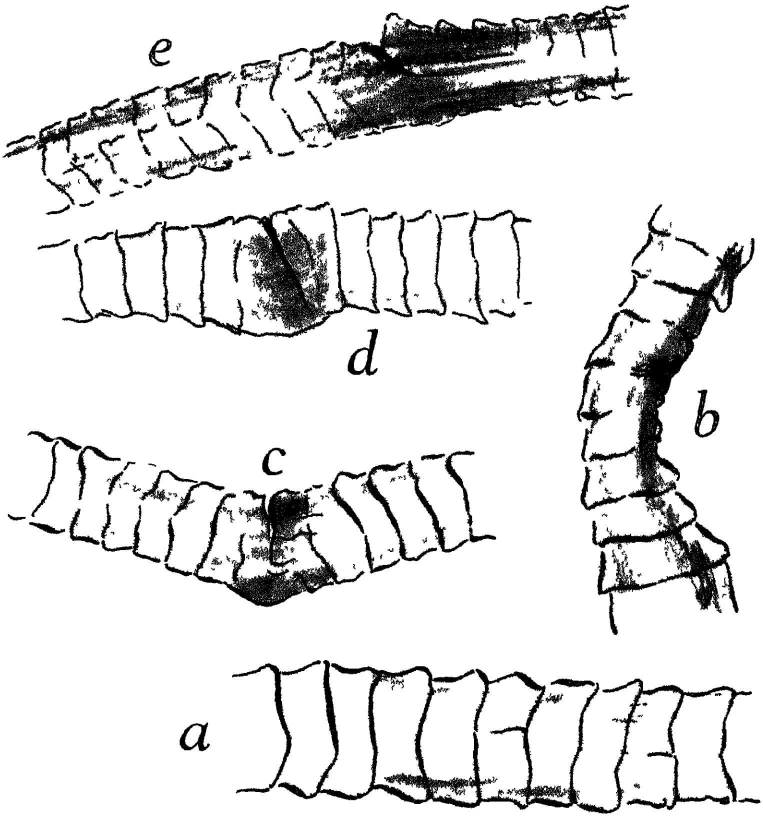


Fig 16
Wool fibres from wool/cotton mixture nightgown , *a* and *b* show Bruising of fibre
c, *d*, *e* Transverse cracking of fibres

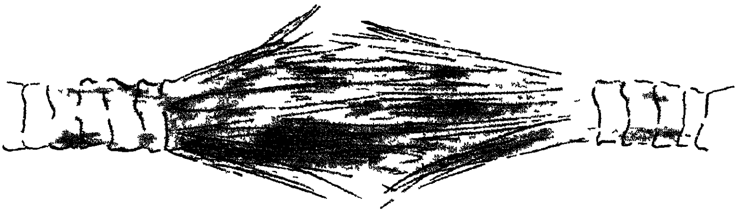


Fig 17
Wool fibre from wool/cotton mixture nightgown showing abrasion The scales have disappeared and the fusiform cells are loosened and protruding

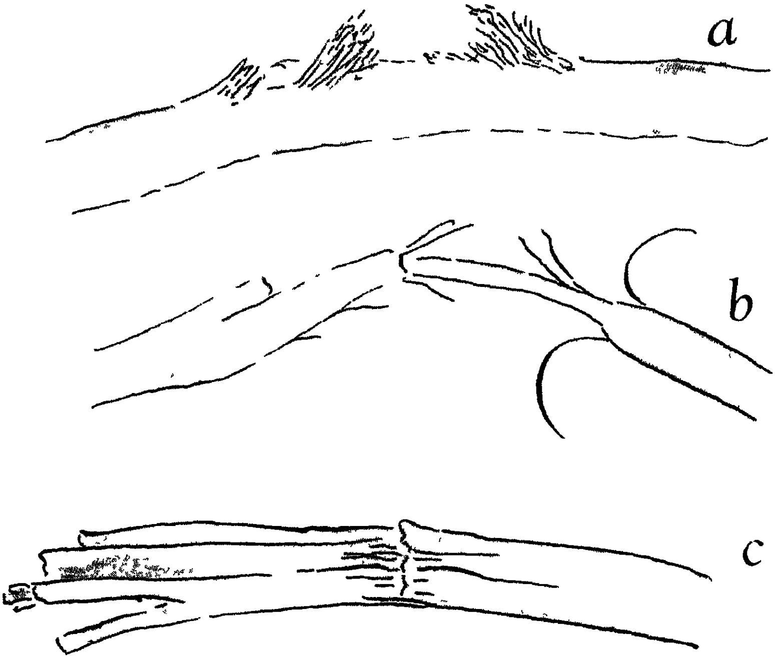


Fig 18
Fibres from spun silk warp of nightdress, *a* Gentle abrasion, *b* Gentle abrasion with tendency to transverse cracking *c* Transverse cracking

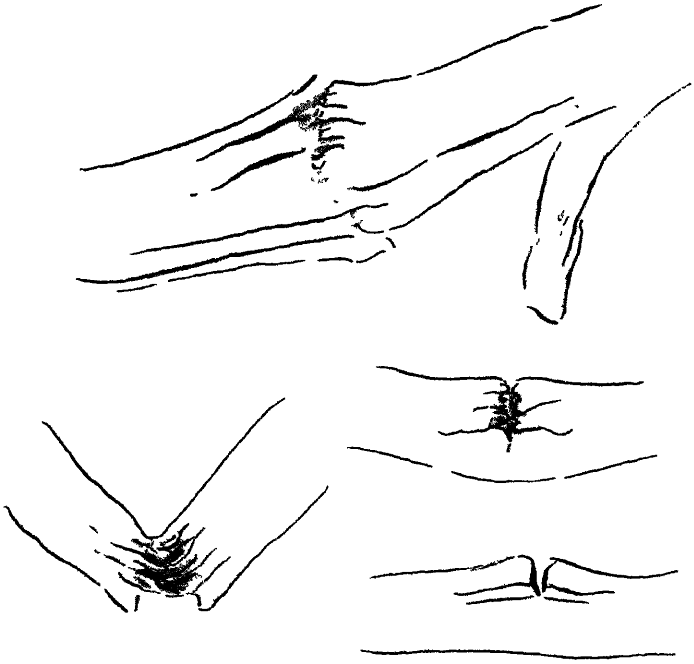


Fig 19
Fibres from net silk weft of nightdress showing transverse cracking.

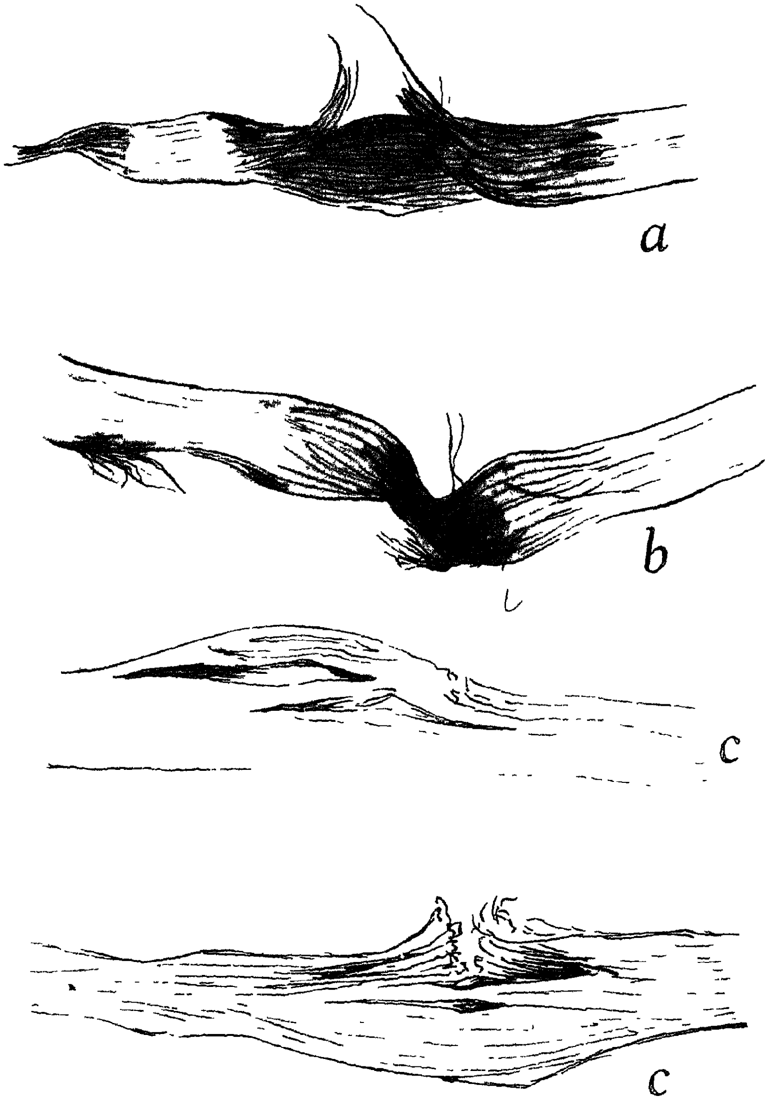


Fig 20

Fibres from tussah silk blouse showing, (*a*) Abrasion, (*b*) Abrasion with tendency to transverse cracking, (*c*) Separation of fibrillae and beginning of transverse cracking

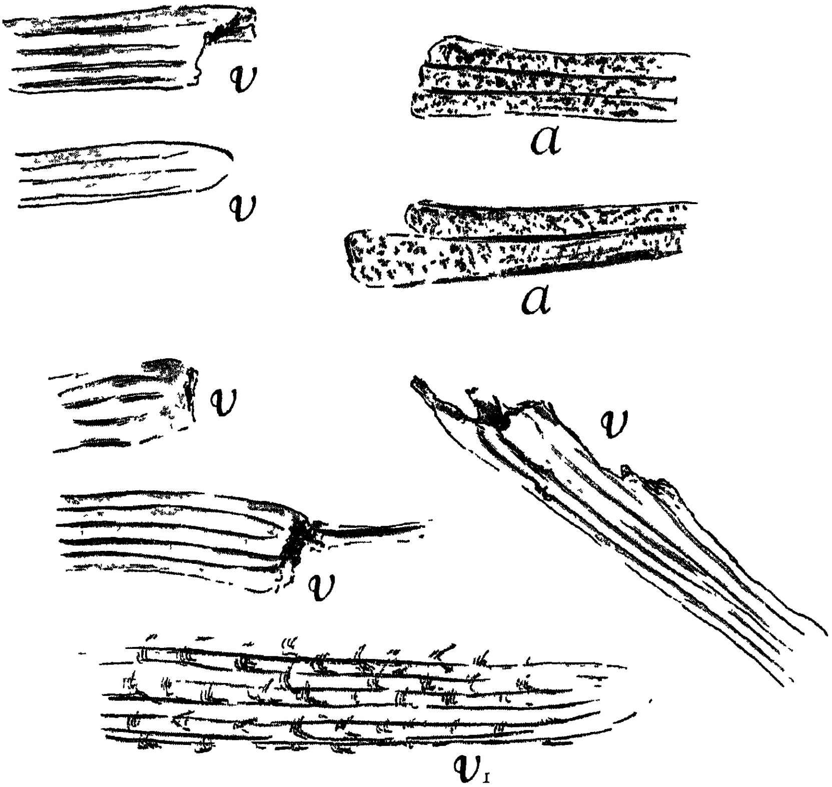


Fig 21
Broken fibre ends from worn cuff of viscose/acetate staple fibre blouse, (*a*) Acetate, (*v*) Viscose
Also fibre from viscose staple fibre shirt showing slight abrasion (v_1)

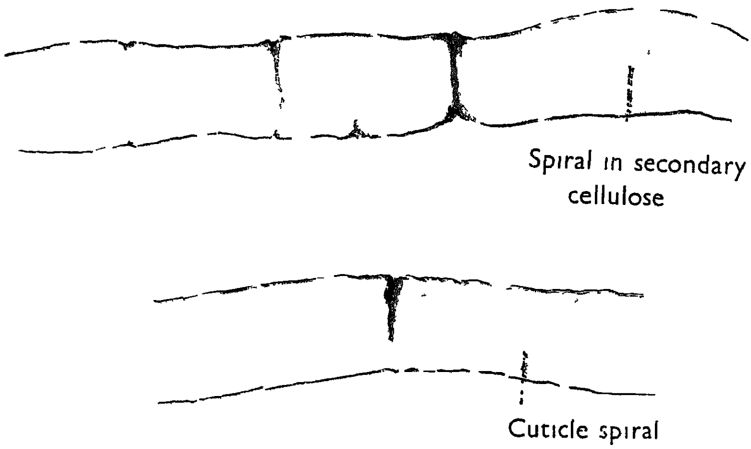


Fig 22
Cotton fibre stained to show cuticle spiral, and transverse cracks
The spiral in the secondary cellulose is also visible

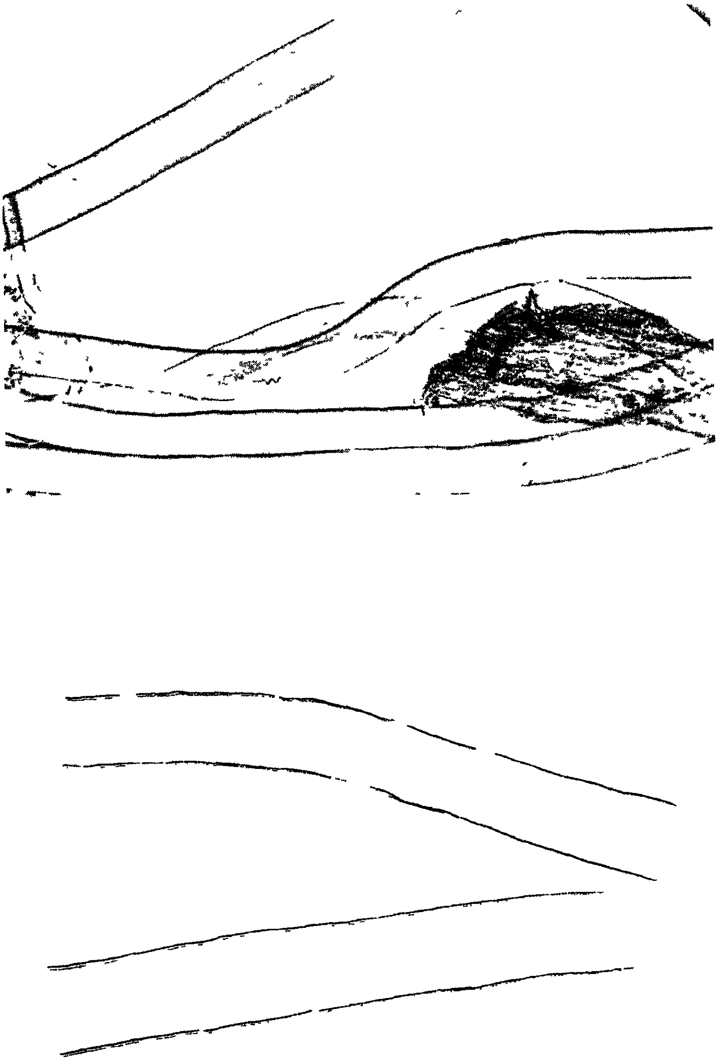


Fig 23
Normal flax fibres on treatment by modified Congo Red staining method

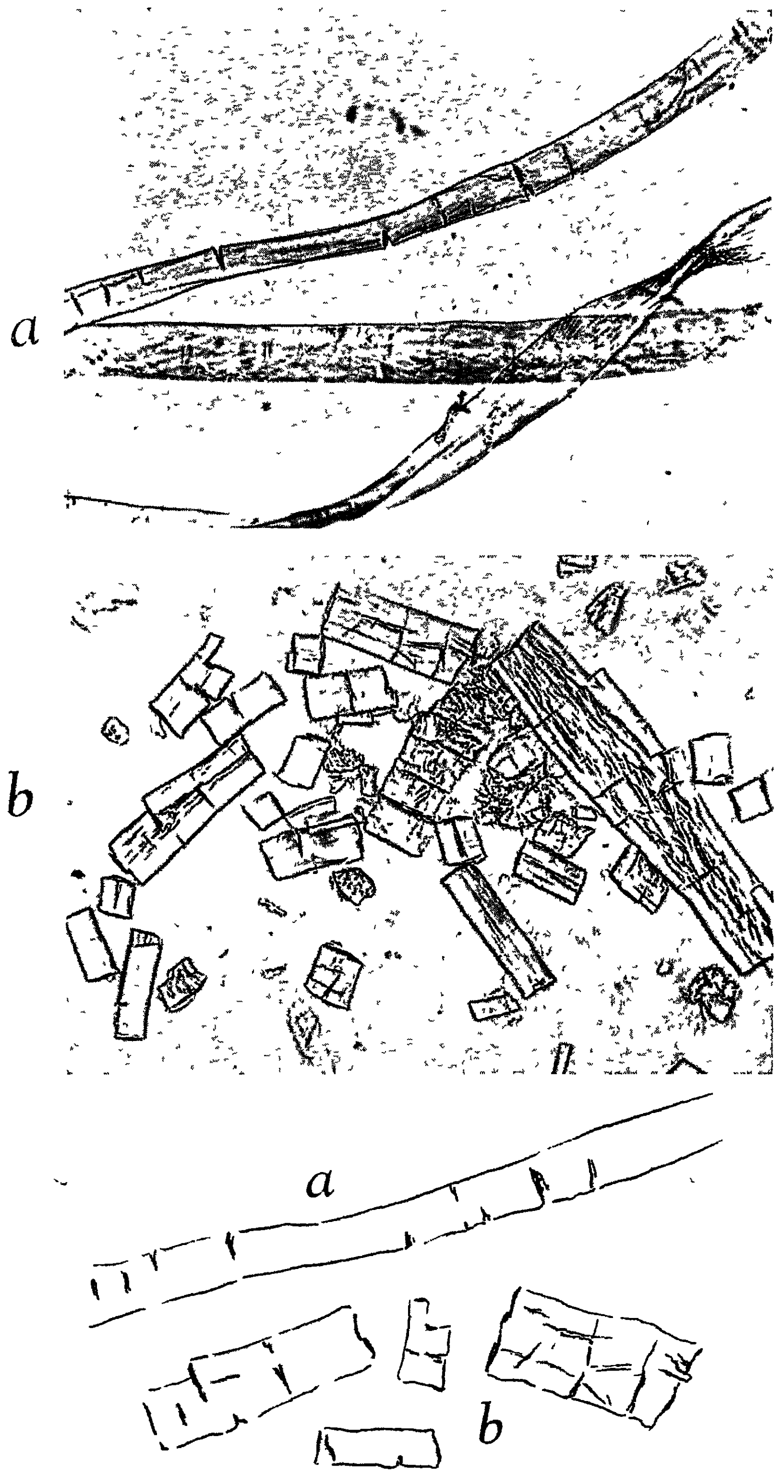


Fig 24

(a) Heat tendered flax fibres } on treatment by modified Congo Red
(b) Acid tendered flax fibres } staining method

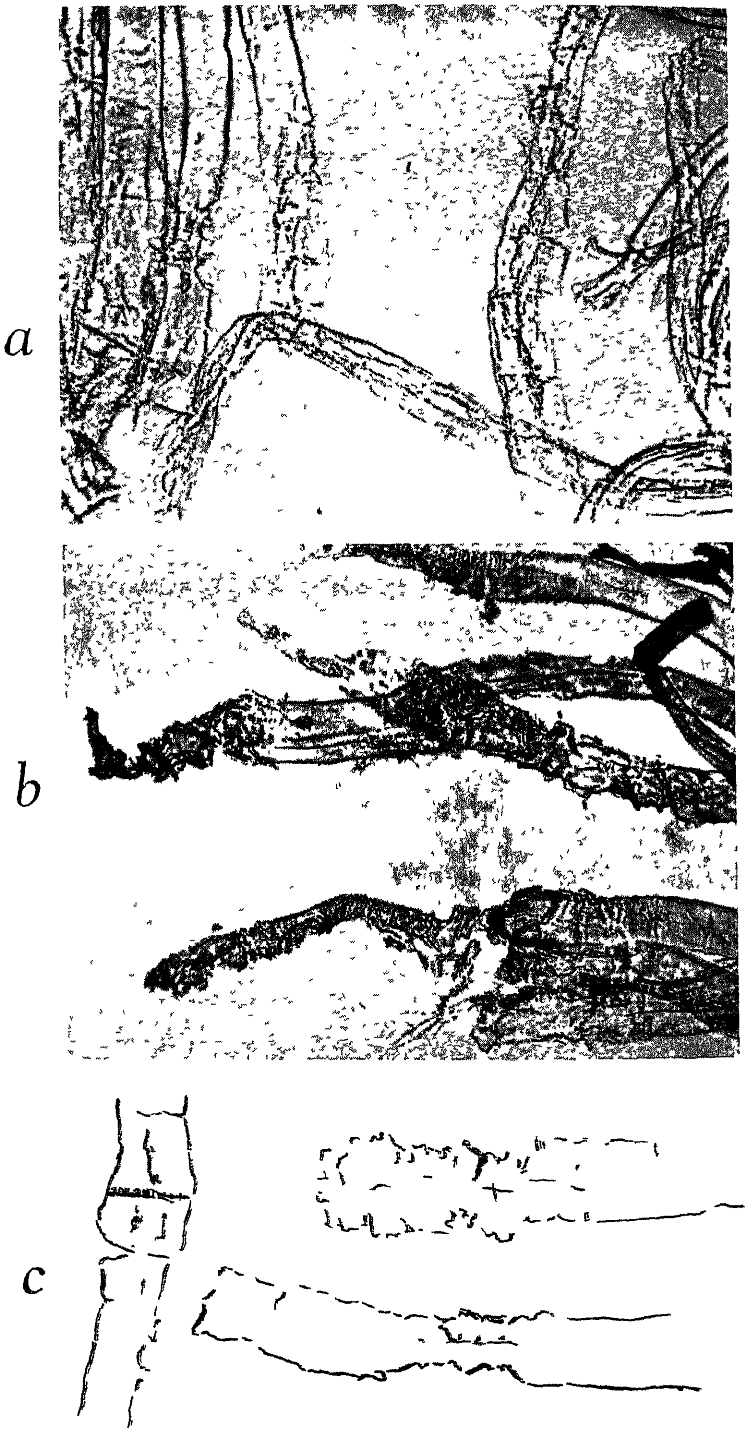


Fig 25
Flax fibres tendered by micro-organisms, on treatment by modified Congo Red staining method

IV. COMPARISON OF COTTON FIBRES FROM WORN GARMENTS AND FROM YARNS AND CLOTHS SUBJECTED TO LABORATORY TESTS

The appearance under the microscope of fibres from cotton cloths which have been tested in a laboratory abrasion testing machine is identical with that of fibres which have suffered abrasion in wear. The conditions of testing on the cloth abrasion test are similar to those suffered by these particular fibres in use, namely abrasion under tension and pressure.

The very gentle abrasion seen in the majority of garments is reproduced by the same machine under conditions modified so that the fabric tested is not held under tension and the fibres are to some extent free to move.

Testing of yarns and fabrics on a machine designed to give repeated sharp flexions of a yarn at one point result in a cracking across the fibres but so far it has failed to produce the preliminary transverse markings and cracks found in the worn garments and articles.

A peculiar appearance is observed in fibres from the binding threads of a camel hair belting. A similar appearance is produced in fibres from heavy canvases tested on the flexing machine The camel hair beltings in question have four plies, each having a camel hair warp and a cotton weft, these plies being united by cotton warp binders. For some years beltings which have failed in use because of the breakdown of the binders have been submitted for examination and have proved a somewhat difficult problem to solve. The position of the breakdown of these binders is localised at the crossing points between the plies and the appearance under the microscope of the damaged and broken fibres after Congo Red staining is depicted in Fig. 12. The explanation of the breakdown was provided when a similar effect was observed in heavy canvases subjected to the Repeated Sharp Flexing Tester. The breakdown can, therefore, be attributed to repeated flexing of the yarns accompanied by some bruising caused probably by a slight play between the plies.

Cross markings and cracks in the fibres have been reproduced, however, in the following manner. Single fibres coated with shellac from alcoholic solution were mounted with wax on an electrically maintained vibrator, such that the fibre moves from an initially straight position to a sharply bent position and back again about 50 times per second. Thus the fibre is bent sharply without direct tension being applied. Sakel cotton fibres (taken from the bale), after several million cycles, showed transverse markings similar to those observed in the fibres from worn fabrics. Mercerised and bleached fibres (fluidity 6 and 21) showed transverse markings after less than one million cycles

V. BREAKDOWN OF LINEN, WOOL, SILK AND RAYON FABRICS IN USE

Franz and Henning[6] state that in addition to abrasion, wool fibres in a cloth are subjected to "ever recurring bending stresses" which cause the fibres to break up. This is in complete accord with the results of the investigation on cotton fibres and in order to discover whether the mechanism or breakdown of all fibres is substantially the same, worn linen, woollen, silk and rayon fabrics have been examined.

A fairly systematic examination has been made of the breakdown of linen fabrics but only a cursory examination has been made of silk, wool and rayon.

LINEN FABRICS

Linen garments and articles which had passed out of service, and worn parts of articles still in use were collected and examined. Included in the examination were sheets, pillow slips, cushion covers, loose cover for a settee, damask table cloths, table napkin and holder, linen dress and blouse, Dodger from the bridge of a ship, hose-pipes, fishing nets, Indian "chagul" (water-holder) and a shirt with a cotton warp and linen weft.

The examination was similar to that for cotton, the mode of breakdown was recorded, the fluidity was determined and the fibres from the damaged and worn portion were examined by the modified Congo Red test, described in the Appendix

Chemical Tendering

The results of the fluidity determinations are given in Table V. No determinations were made on the linen garments with a urea formaldehyde crease resistant finish nor on those articles which gave evidence of intense biological tendering.

With the exception of those articles which have suffered definite chemical tendering in use, i.e. sun-blinds and Dodger, the rise in fluidity does not account for the weakness of the fabric.

Table V

Fluidity of Worn Linen Articles

	Fluidity		Fluidity
Settee cover	8	Sunblinds . . .	20–37
Cushion covers ..	14	Dodger from a ship .	25
Handkerchiefs	18	Table napkins .	21–23
Sheet ...	27	Napkin holder	26
Table cloth	28		

Mechanical Breakdown

(1) *Fibre Abrasion.*

Fibre abrasion to any appreciable degree is found only in the fibres from the damask table cloth (Fig. 13). Like the cotton articles in which intense fibre abrasion is found, the cloth had been heavily starched and the fibres were firmly held by the starch. Much of the abrasion is probably due not to wear in use, but to the calendering necessary to produce the highly glazed finish.

(2) *Transverse Cracking of the Fibres*

With the exception of the table cloth, the mechanical breakdown of the linen fabrics and articles is due entirely to transverse cracking of the fibres. Worn portions of settee covers, cushion covers, handkerchiefs, sheets, linen frock and blouse (under-arm wear) all show segmentation and breakdown of fibres due to transverse cracking and an almost entire absence of fibre abrasion (Fig. 14).

This is shown in a striking manner in the fibres from the holes in the under-arm of an anti-crease linen frock Although the appearance of the hole is suggestive of fibre abrasion, the fibre ends show only a break up due to transverse cracking, and evidence of fibre abrasion is entirely absent (Fig. 15) The fibres from a settee cover (fluidity 8) which had broken into holes along the front of the seat, the appearance of which again is indicative of abrasion, show only transverse markings and break up, no evidence of fibre abrasion is found.

WOOL GARMENTS

A few worn wool garments have been examined (cotton/wool mixture shirts and pyjamas, wool vests, children's frocks, nightdresses) all of which had been carefully washed and had passed out of service owing to breakdown.

Microscopical examination of the fibres was carried out after treatment with Shirlastain A for five minutes.

Examination of a Worn Cotton/Wool Mixture Shirt

A shirt, 2 × 2 twill, woven from yarns spun from a mixture of approximately 50 per cent. wool and 50 per cent. cotton, handed in as unserviceable.

shows similar features to the worn cotton shirts, i.e. wear at the cuffs and collars, and extreme weakness in both the warp and weft directions and with a long slit at the back caused by breakdown of the weft. Staple diagrams of the fibres pulled down from the warp and weft yarns show breakdown in staple similar to that obtained for the worn cotton shirts. The results are given in Table VI together with the results of stapling tests on the original yarn.

Table VI

	Worn shirt		
	Warp	Weft	Original yarn
Effective length	32	18	44
% Short fibre	61	63	36

The fabric before stapling had been dyed with an acid dye to make a colour differentiation between the wool and cotton. A fairly even distribution of the two fibres in the staple diagram is found. It would appear from this that this break up of the fibres obtains for wool to the same degree as for cotton.

Chemical Deterioration.

The fluidity of the cotton in the wool/cotton mixture was determined,* and the figure of 12·7 obtained shows only slight chemical deterioration. Staining tests on the wool provide evidence of only slight chemical degradation.

Mechanical Breakdown.

Although in chemical nature and physical structure the wool fibre differs considerably from the cotton fibre, it has certain features in common—protective scales which correspond to some extent with the cuticle of the fibres, the fibrous cortex consisting of spindle-shaped cells, corresponding to the secondary cellulose with its fibrillæ. Shirlastain reacts with wool in a similar manner to Congo Red with cotton, staining the cortex, if the scales are loosened or damaged, but no pre-treatment is required. The majority of the wool fibres from the cotton/wool shirt show mechanical damage at a number of places along their length. This ranges from bruising of the fibre, shown as a staining of the cortex with only slight, or in some cases, no obvious damage to the scales (Fig. 16*a* and *b*), to intense abrasion revealed by absent and damaged scales with the loosened and protruding spindle-shaped cells of the cortex stained a deep brown (Fig. 17).

Transverse cracks and fissures are found, accompanied by very localised staining (Fig. 16*c*, *d*, *e*), and the majority of the broken fibre ends give very little evidence of abrasion. No preliminary cross markings are found. Woollen vests, union pyjamas, and children's frocks examined show the same features of mechanical breakdown.

(C) SILK GARMENTS

Two worn silk nightdresses made from crêpe silk having a two-fold spun silk warp, and a net silk crêpe weft were examined.

The garments had been worn by a bed-ridden owner and had passed out of service chiefly because of large splits warp-way and weft-way in the fabric at the back below the waist, and extreme weakness of the fabric in the neighbourhood of the splits.

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* The wool was dissolved by treating 0·4 g. of the finely cut up material with 20 c.c. of 5 per cent. sodium hydroxide solution at room temperature for one hour. The undissolved cotton was filtered on a sintered glass filter and washed successively with a further quantity of solvent, dilute acetic acid, ammonia, and water, and dried. The fluidity was then determined in the usual way.

Chemical Deterioration

The fluidity of the silk in cupri-ethylenediamine was determined and figures of 21·4 and 23·6 were obtained for the warp and weft, respectively These account for a drop in strength of approximately 25 per cent

Mechanical Breakdown

The silk fibre, after removal of the sericin or silk gum, still retains a protective layer covering the fibroin. Mechanical damage to a silk fibre may be shown by staining with Congo Red after immersion for about one minute in 18 per cent. caustic soda solution. The surface layer stains only a faint pink but where the surface layer is damaged or ruptured the fibroin stains a deep pink or red

The yarns from the nightdresses were pulled down and show considerable break up of the fibres The warp has a high crimp and a much softer twist than the weft which it tends to cover. The warp crowns break down and are removed in a similar manner to the crowns in the cotton poplin warp. The fibres from these crowns give evidence of abrasion of a fairly gentle type (Fig. 18*a*). Transverse cracks may be seen in the weft fibres and are obviously responsible for their break up (Fig 19). They occur to a much less degree in the warp (Fig. 18*c*). In neither the warp nor the weft is there any evidence of preliminary transverse markings

The worn portion under one sleeve removed from a tussah silk blouse, which showed considerable evidence of wear but had not passed out of service, was examined. Tussah silk fibres fibrillate easily and the damage in most of the fibres is shown as a rubbing up of the fibrillæ (Fig. 20). There is, however, some evidence of a separation, and cracking across the fibrillæ, probably due to bending stresses (Fig. 20*c*).

(D) VISCOSE RAYON

Garments and articles woven from spun mixtures, a spun viscose rayon shirt, shirts made from mixture yarns of viscose rayon and wool, worn cuffs from a spun viscose and acetate rayon mixture blouse, all of which had passed out of service have been examined and have shown very little evidence of fibre abrasion The continuous filament yarns show a definite tendency for the filaments to be rubbed or pulled out of the cloth and broken.

The staple fibre in the warp and weft of the shirts shows a fibre breakdown very similar to that obtained for the cotton poplin shirts. The warp crowns show successive break up of the fibres and there is evidence of some slight abrasion. The general tendency, however, is for the fibres to break transversely and this is often accompanied by some fibre distortion. The worn cuffs of the spun mixture blouse show similar features (Fig. 21).

VI. NATURE OF CROSS MARKINGS AND CRACKS

This examination of worn fabrics has shown that all the fibres examined —cotton, linen, wool, silk, viscose rayon—break at right angles to the long axis of the fibre, as a result of wear, and that the cotton and flax show some preliminary cross markings.

In none of the fibres does there appear to be any relation between the inclination of the fibrillæ and the lines of segmentation. Fig. 22 depicts a cotton fibre stained to show the slow spiral of the cuticle and the quick spiral of the secondary cellulose is also seen. The stained fissure cuts across both spirals, obviously bearing no structural relation to either.

The cross markings in the flax fibres are undoubtedly a further stage in the dislocation marks which are characteristic of bast fibres in general These again are at right angles to the long axis of the fibre whereas there are two sets of fibrillæ in the bast fibre, an outer flat right-handed spiral inclined at an angle of about 70°, and an inner left-handed spiral inclined at an angle of 5°.

The fibrillæ of wool and silk are dispersed slightly, but tend to lie along the main axis of the fibre. The limited examination of these fibres has shown that they break transversely in use, but the breaks are neither as sharp as, nor as definitely at right angles to, the axis of the fibre as those in cotton and flax.

The break up of both the continuous rayon fibres and the viscose staple fibre resemble the ends of broken glass rods, ranging from a clean break across to irregular breaks with jagged edges (Fig. 21).

CONCLUSION

The investigation has shown that although textiles in service undergo a varying amount of chemical deterioration through laundering, exposure to light, and atmospheric conditions, failure is mainly due to a weakening of the structure caused by mechanical breakdown of the individual fibres and that the mechanism of breakdown is substantially the same for all fibres, cotton, wool, linen, silk, and rayon. Only those fibres held firmly by tension, pressure or filling suffer intense abrasive action The breakdown of a large proportion of the fibres is caused by transverse cracking, which judging by the location of the position of maximum weakness in the textiles examined, is the direct result of flexing and bending stresses suffered during wear. Fibres on the surface which are only lightly held suffer a gentle abrasive action.

The general weakening of the fabric structure and the majority of the tears and splits which occur in many worn garments are a direct consequence of this fibre breakdown.

APPENDIX

MICROSCOPICAL EXAMINATION OF TENDERED LINEN

During an investigation on the substitution of cotton for flax in the manufacture of canvases, the question arose of the comparative susceptibility to biological attack of the two fibres, cotton and flax. The information obtained from the literature on the microscopical tests available for the detection of biological attack on flax was so scanty that a thorough investigation on the tendering of flax was found necessary Chemical and mechanical tendering in addition to biological tendering were investigated, since knowledge of all types was found necessary to form a reliable diagnosis.

A microscopical method for distinguishing between the main types of tendering has been worked out, which is simple and may be used by anyone who has a working knowledge of the microscope. The enquiry set out to distinguish biological from chemical or mechanical tendering, and although some difficulty may be experienced in deciding by microscopical means alone whether weakness is due to chemical tendering or mechanical flexing, no difficulty should be experienced in recognising biological tendering. The information may or may not be known to microscopists who have had to work with flax, but so far as is known it has not been published

Method

The fibres are successively immersed in an 18 per cent. solution of caustic soda for about 3 minutes, washed, stained in a saturated solution of 2 per cent. Congo Red for 1 minute, washed and mounted in 18 per cent. solution of caustic soda

Appearance of Fibres after this Treatment

I. *Normal Untendered Fibres*

A normal untendered fibre treated in this way is stained a faint pink, the cross markings show faintly and there is no transverse cracking or segmentation (Fig. 23).

II *Chemical Tendering.*

(*a*) *Strong acid tendering.* Flax fibres which have been tendered chemically to the point of being very obviously weak, break sharply into transverse segments when treated with 18 per cent caustic soda solution and there is a tendency to break up longitudinally, thus producing a number of small rod-like structures This is shown in Fig 24*b* which depicts fibres taken from a table cloth, tendered by treatment with 5 per cent. sulphuric acid followed by drying in a warm atmosphere.

(*b*) *Effect of bleaching* A set of samples bleached to different fluidities were treated and examined The samples were not sufficiently large to determine their strengths.

Table VII

	Fluidity
Original yarn 25, line D W D R	—
CT 39	1·5
40	5·7
41	9·0
43	16·0
45	25·0
Original yarn 25, Tow BX	—
CT 16	2·5
38	20·0

The fibres in all the samples stain a faint pink only and the cross markings are scarcely visible. The samples CT 38 and 45, which give fluidity figures of 20 and 25, respectively, show some transverse splitting in a small proportion of the fibres (Fig. 24*a*).

III. *Heat Tendering*

A set of samples of yarn, grey scoured, and grey extracted, were heated at a temperature of 150° C. for periods varying from 16-112 hours Fluidity measurements and yarn strengths were determined and are shown in Table VIII. It will be seen that heating the fibres for 112 hours reduces the strength to about 25 per cent. of the original.

Table VIII

Material	Sample No	Time of heating at 150°C	Breaking load, grams	Fluidity
Grey linen	F. 1 e	Nil	977	2·5
	f	16	731	
	g	31	627	18·1
	h	65	463	
	i	112	255	31·5
Scoured linen	F 3 e	Nil	775	5·4
	f	7	619	
	g	16	570	12·4
	h	31	488	
	i	65	355	20·0
Extracted grey linen	F 4 a	Nil	910	2·9
	b	31	601	
	c	112	288	30·9

Examination of the fibres under the microscope after swelling and staining shows that the reactions are similar to those of the bleached fibres and transverse splitting is shown only in F1. h, F1 i, F3. i, F4 c, which give fluidity figures ranging from 21-31.

This transverse splitting in both the bleached and heat tendered samples is very sharp and the slight markings visible are only faintly stained by the Congo Red

IV *Mechanical Damage.*

Examination was made of several linen pillow slips and cushion covers which had been tendered in use to such a degree that cracks and holes had appeared. Fluidities were determined and these ranged from 13 9 to 19·1 On examining the fibres under the microscope after swelling and staining *bright red cross markings* are visible and cracking occurs along many of the markings (Fig 14*a*). These crackings are not so clean cut as those seen in the chemically-tendered fibres, and under high magnification are seen to have a saw toothed edge (Fig. 14*c*).

V *Biological Tendering*

The samples examined were as follows.—

(*a*) Unbleached linen fibres from canvas tendered by placing in soil in a humidified cubicle

(*b*) Hose-pipe tendered by micro-organisms.

(*c*) Indian "chagul" (water container, made of linen)

(*d*) Fishing net

The fibres from all these samples show a faint pink staining only and irregular transverse cracking. This is shown in Fig. 25*a*, *b* and *c*, and although there is some variation in the appearance of these biologically tendered fibres the appearance is very characteristic and cannot be confused with either chemical or mechanical damage.

The procedure for determining the cause of tendering is as follows·—

General Tendering

First determine the fluidity,[1] the figures given in Tables VII and VIII for fluidity and strength should provide a sufficient guide as to whether the tendering is chemical in nature If the fluidity figure gives no indication of chemical tendering, examine under the microscope after swelling in caustic soda solution, 18 per cent , followed by Congo Red

(*a*) *Bright red* transverse markings with a tendency to break up along them indicate weakness due to *mechanical flexing.*

(*b*) Irregular transverse segmentation indicates biological tendering and this should be confirmed by staining for the presence of bacteria or fungi

The fluidity figure may indicate tendering, but may not be high enough to account for the weakness of the fibre, in which case a microscopical examination is necessary since the tendering may be localised on the surface, or mechanical flexing damage may be present in addition to chemical tendering

Local Tendering

It may be possible to determine the fluidity of the tendered portion if it is not too small, if there is a hole, the fluidity of the material adjacent to the hole may be found

In addition, the tendered portion or the broken yarn ends from the hole should be examined microscopically and the reactions obtained for the different types will be similar to those for general tendering

The reactions are summarised in Table IX.

Table IX

1 Raw fibre ..	Faint cross markings (Fig. 23)
1a. Raw fibre, heat treated	Ditto—*fissures begin to appear* at fluidity of 20 approximately (Fig. 24).
2 Bleached fibres	*Cross markings not obvious* *Fissures began to appear* at fluidity of 20, approximately
2a. Bleached fibres, heat treated	Ditto
3 Fibres tendered by	
(*a*) Mechanical flexing, use, or processing	*Cross markings* bright red and cracking seen along these Under high magnification markings have toothed appearance (Fig 14 *a, b, c*)
(*b*) Fibre abrasion ...	Abrasion obvious Cross markings only faint (Fig 13)
4. Biologically tendered fibres ..	Fibres show *irregular transverse cracking* (Fig 25 *a, b, c*)

REFERENCES

[1] Clibbens and Geake *Shirley Inst Mem*, 1927, 6, 117 or *J Textile Inst*, 1928, 19, T77
[2] Bright. *Shirley Inst Mem*, 1926, 5, 141 or *J Textile Inst*, 1926, 17, T396
[3] Clegg *Shirley Inst Mem*, 1940, 17, 63 or *J Textile Inst*, 1940, 31, T49
[4] Clibbens and Ridge *Shirley Inst Mem*, 1928, 7, 85 or *J. Textile Inst*, 1928, 19, T389.
[5] Clegg *Shirley Inst Mem*, 1932, 11, 1 or *J Textile Inst*, 1932, 23, T35
[6] Franz and Henning *Textilberichte*, (English Edn), 1937-38, 19, 1.
[7] Garrett and Howitt. *Shirley Inst Mem*, 1940, 17, 103 or *J Textile Inst*, 1941, 32 T1.

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29—LAMINATED TEXTILES AND SIMILAR MATERIALS: A BALLISTIC METHOD FOR THE DETERMINATION OF INTER-PLY ADHESION

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SUMMARY

For use on laminated textiles, a ballistic method for the determination of inter-ply adhesion has been evolved. It consists of the measurement of the work expended in separating the plies and makes use of a ballistic testing machine to this end.

Tests on several plied fabrics have shown that the work done in peeling bears a linear relation to the area peeled and that the curve passes through the origin. A unit measure is proposed. This is a ballistic peel factor which is numerically equal to the work necessary to separate the plies in one square inch of compound fabric

Exploratory tests on several adhesive/adherend systems indicate that the method is capable of extension to the larger and more varied field of general adhesives. Results on adhesive tape/sheet metal, fabric/adhesive/sheet metal and metal foil/adhesive/metal foil systems are quoted.

INTRODUCTION

Laminated textiles have recently become more widely used, sometimes instead of the multi-ply woven article. A typical example is the replacement of the compound woven collar cloth[1] by the Trubenised-type of collar. Other examples of laminated textiles in everyday use are rubber belting (from 2- to 8-ply), motor-car hood fabrics (coarse robust outer-ply with fine decorative inner-ply) and golf and similar bags (duplex wigan or duck) Haven[2] gives two lists of textiles which include many laminated fabrics

Whether the laminated textile is a new product or is intended to replace a compound-woven fabric is immaterial in so far as some measure of the inter-ply adhesion is usually required. It is seldom possible so to arrange the manufacture of a composite article that the adhesive will never be subjected to any load other than one of shear. Even if such were possible, casual circumstances might arise where resistance to peeling, or separation of the plies, would be a desirable property of the laminated fabric. Apart from these considerations, some form of peeling test is often necessary to enable distinctions to be made between several adhesives which, when tested in shear, are stronger than the fabric

Peeling tests to assess the inter-ply adhesion appear so far to have taken one of two forms They have been either (i) an estimate of the speed with which the plies may be separated when an end of one ply has been lifted, sharply doubled back upon itself and then weighted, or (ii) where the maximum or average load necessary to separate the plies in a given area of laminate has been measured.

The rate of separation test has been fully described in a number of official British specifications Various arbitrary units are employed therein as shown below.

Width of test piece—2 inch, 50 mm , 60 mm
Applied load—1 to 7 lb. and 1 5 to 3 5 kg
Maximum distance separated—¼ inch and 5 mm.
Time of load application—5 minutes

In the peeling test a piece of fabric of known width has its constituent plies partly separated. A definite length of the cloth is left in the normal state, *i e* with the plies not separated. Using an orthodox tensile test method the load necessary to effect complete separation of the plies in the known area of cloth is measured So far as is known, this method is not specified in any British specification However, one American specification[3] describes such a method and calls for the testing machine to be autographic with the maximum load indicating device out of action. Thus a fluctuating trace is produced and the specification states that this chart constitutes the report, but the value of the adhesion shall be determined by drawing the best average' line between the maximum and minimum load values.

In testing adhesives generally, methods of measuring resistance to peeling appear to have received little attention, apart from the glass plate/varnish and lacquer/silk cloth technique described by Ellis[4] and the glass plate/adhesive/paper system.[5] The method now proposed to measure the resistance to peeling at high speeds may therefore be useful to those engaged in the testing of adhesives generally. It should be particularly applicable in certain circumstances [6]

EXPERIMENTAL

Proposed New Method of Assessment

A two-ply fabric, composed of two dyed 8 oz /sq yd cotton fabrics with an inter-ply layer of a cellulose ester, was tested by methods of (i) and (ii) above By the rate of separation method, peeling occurred in the warp direction at average rates varying from 1 35 to 2·55 in /min. and in the weft direction at 0 45 to 1 50 in /min Peeling load tests as measured by the maximum load indicating pointer produced results which were less variable, but it was appreciated that these were chiefly a measure of the peak resistance to peeling The American fluctuating trace method would appear to overcome this difficulty since it registers depressions as well as peaks. Measurement with a planimeter of the area between the trace and the elongation axis might be used to obtain a " best average line between the maximum and minimum load values" or might even permit the assessment of the work done This caused consideration to be given to a test method which would automatically measure the work done and thus give a rapid over-all measure of the resistance to peeling

Instead of using an ordinary tensile testing machine for the maximum peeling load determination, use was made of the ballistic testing machine marketed by Messrs Goodbrand & Co Lengths of plied fabric were cut ½, 1, 1½ and 2 inches wide The test specimen length was so chosen that when the plies were separated and gripped in the jaws of the testing machine, a known length remained to be peeled, and the peeling began as the pendulum bob passed through its lowest position. All the test specimens were conditioned for at least 48 hours in an atmosphere controlled at 65 per cent relative humidity and 70° F , the actual tests being made under these conditions. The amount of energy spent in completely separating the plies was noted by reading the calibrated scale of the testing machine

This figure represents the work done on the whole length of the test specimen between the machine grips It may be considered to have three components—(*a*) the work necessary to overcome the adhesion between the two plies, (*b*) the work spent in stretching the tails of the test piece, and (*c*) the work expended in flexing the fabric during the peeling operation

The majority of fabrics may be considered as infinitely flexible so that item (*c*) could be neglected. Item (*b*) can be eliminated by considering the work done in peeling to be the difference between the results on two test specimens of different sizes, *e g* (work done in peeling 2 inches long by 1 inch wide) minus (work done in peeling 1 inch long by 1 inch wide) gives the amount of work done in peeling an area 1 in × 1 in A somewhat similar process has previously been used by the British Cotton Industry Research Association when using a ballistic machine to assess the tearing strength of fabrics

A 3-ply rubberised fabric, used for gas-retaining purposes, was tested by this method Test specimens were cut normal to the longitudinal direction of the roll and the back ply was peeled away from the other two plies The inter-ply adhesive was natural rubber and tests were made with the ballistic pendulum testing machine Some typical results are quoted in Table I to illustrate the recorded observations. The majority of the test results are given in the form of graphs

Table I
Plied Rubberised Fabric
Detailed results on one inch wide test specimens

Length peeled	½ in	1 in	1½ in	2 in	2½ in	3 in
Actual machine readings (inch-pounds)	11 13 12 13	22 21 22 23	29½ 30 29 30	43 45½ 41 38	51 46½ 46½ 47	58 56 56½ 55
Mean	12½	22	29½	42	48	56½

Work done in peeling
½ in length (1″–½″ , 1½″–1″ , 2″–1½″ , 2½″–2″ and 3″–2½″) gives a mean of 9 inch-pounds
1 in length (1½″–½″ , 2″–1″ , 2½″–1½″ and 3″–2″) gives a mean of 17½ inch-pounds
1½ in length (2″–½″ , 2½″–1″ and 3″–1½″) gives a mean of 27½ inch-pounds
2 in length (2½″–½″ and 3″–1″) gives a mean of 35 inch-pounds.
2½ in length (3″–½″) gives 44 inch-pounds

The full results are shown graphically in Figures 1 and 2 In the former the means of the actual machine readings are given. Fig 2 shows the result of plotting the work of peeling against the area peeled. It is obvious that a linear relation exists between the work of peeling and the area peeled, and that the straight line in Fig. 2 passes through the origin of co-ordinates. This enables a single factor to be proposed to characterise the resistance to peeling as measured by the ballistic pendulum. It is now suggested that this be named the "Ballistic Peel Factor" and defined as the work required to separate the plies in a unit area If the area is given in square inches and work in inch-lb , the ballistic peel factor is numerically equal to the work necessary to separate by peeling the components of one square inch of the laminated fabric

Comparative Results on Other Plied Fabrics

A material similar in construction to the gas-retaining fabric, but with a synthetic rubber inter-ply instead of natural rubber, was tested User experience had indicated that the synthetic laminate failed more readily than the one with natural rubber The sampling arrangements and methods of test were as described for the plied fabric which contained natural rubber and the results are given in Fig 3 Thus the ballistic test method indicates that the work necessary to separate the plies bound by the synthetic adhesive is some 20 per cent. less than that required by the natural rubber.

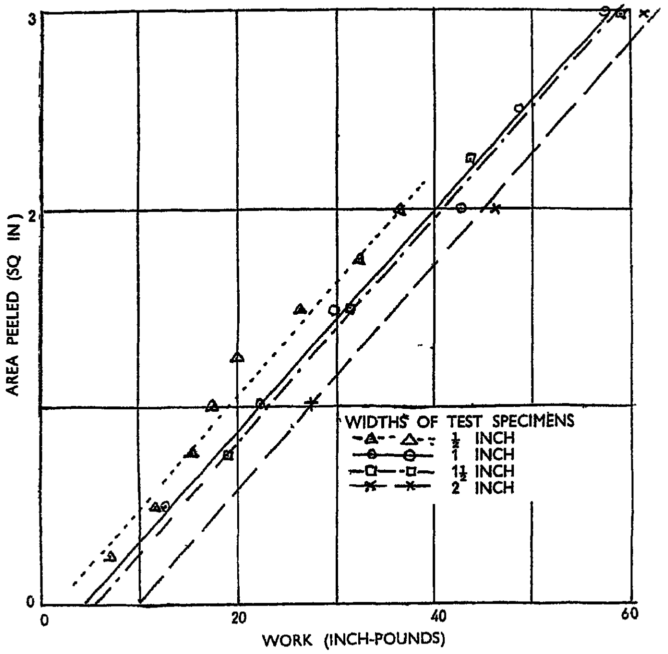

Fig 1

Fabric laminate with rubber interply (means of machine readings)

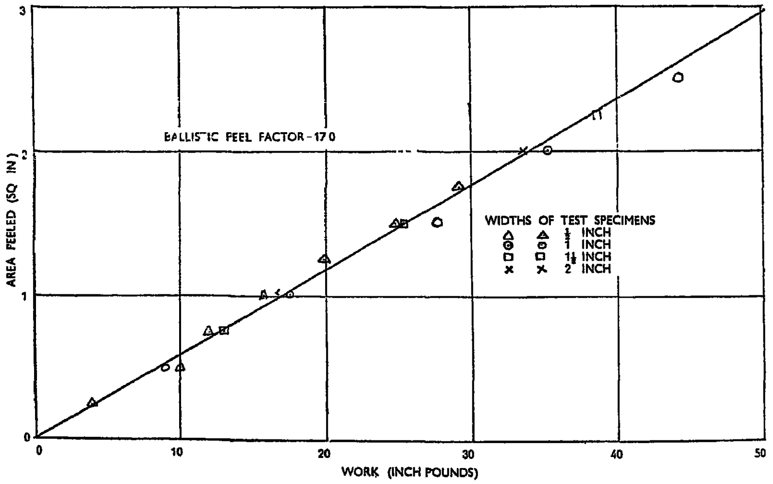

Fig 2

Fabric laminate with rubber interply

Another material tested was a two-ply proofed fabric with a cellulose derivative adhesive The test specimens were cut normal to the longitudinal direction of the roll, *i e* weftwise No unusual features are presented by Fig 4 in which the results are given.

A laboratory-made two-ply cellulosive derivative laminated fabric was assembled in order to test the generality of the ballistic method It was thought that, by comparison with machine-spreading, the laboratory spreading of the adhesive would be irregular and thus disturb the linear relation

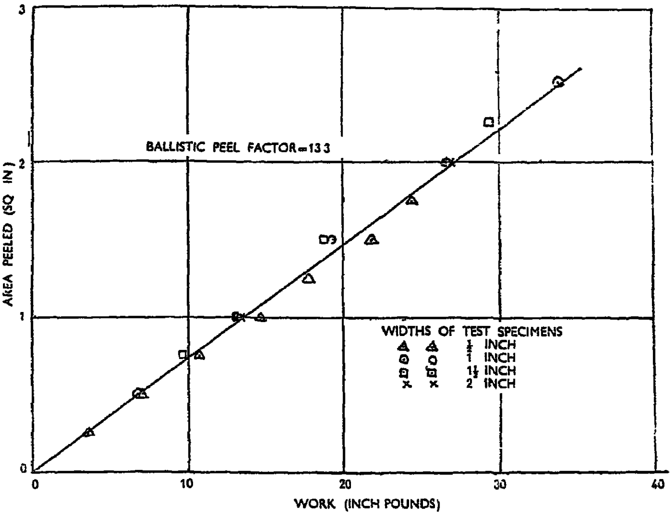

Fig 3
Fabric laminate with synthetic rubber interply.

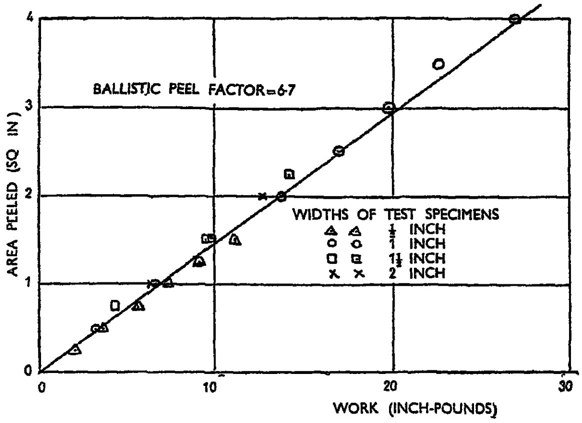

Fig 4
Fabric laminate with cellulose derivative interply

between work required and area peeled The resultant plied fabric was rather stiff, but it was sampled so as to obtain the maximum possible number of inch-wide test specimens The ballistic peel test results are given in Fig 5 It should be noted that although the factor is much lower than that of the other cellulose derivative (Fig. 4), the linearity of the work-area relation remains.

Application of the Ballistic Test Method to Other Materials

For systems consisting of rigid and flexible components such as adhesive tape stuck to sheet metal, all that is necessary is to arrange for the flexible ply to be attached to the pendulum grip and the rigid component to the fixed grip of the testing machine. The flexible component of the test specimen should be long enough to allow the pendulum to be raised to its highest position and for peeling to begin as the pendulum bob swings through its lowest

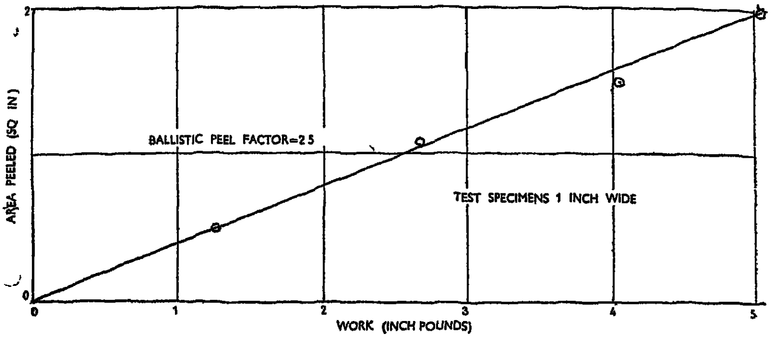

Fig. 5
Hand-made fabric laminate with cellulose derivative interply.

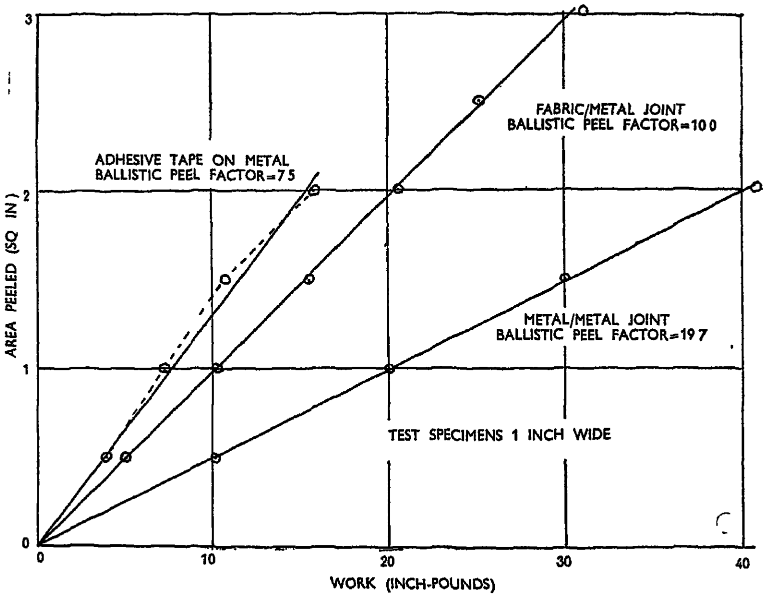

Fig. 6
Results of miscellaneous tests

position. As in the laminates made from two flexible components, the plies are separated except for the known area to be peeled.

At present the test method will not cater for two rigid adherends However, certain materials which are rigid may be made sufficiently flexible by decreasing the thickness. Provided that the thinned materials have surfaces with properties similar to those of material of normal thickness it seems reasonable to assume that the ballistic method will measure the work necessary to overcome the adhesion

Some Illustrative Results on Other Materials

Fig 6 contains the test results obtained on a system consisting of a metal to metal joint The metal was copper foil, 0·0024 in thick, and the adhesive was a rubber-bitumen compound The adhesive was applied to 1 in. wide strips of the foil and the two coated surfaces were brought together The test specimens were prepared and tested as described above Examination of the peeled ends of the test specimens revealed an almost continuous film of adhesive still intact on both adherends. This might indicate that failure was caused by the internal cohesion of the adhesive being less than the adhesive force between adhesive and adherend, but it certainly indicates that flexing of the adherend had no serious effect on the adhesion between adhesive and adherend. The particular adhesive was a readily deformable material when set—a factor which, according to the reasoning of Rivlin,[7] may account for the relatively high ballistic peel factor

Representative results obtained with a rigid/adhesive/flexible system are also given in Fig. 6 In this case, rubberised fabric was stuck to 24 SWG Duralumin with a rubbin-resin compound. This adhesive was hard when set—in contra-distinction to that used on the metal foil system.

Tests were also made by the foregoing method on adhesive tape and the results will be found in Fig. 6. The tape which was available was one inch wide and readings for peeling distances of 1, 1½, 2, 2½ and 3 inches were obtained The rigid adherend was sheet Duralumin. Points on the graph, which are the net readings, are more dispersed than in any of the other systems tested.

DISCUSSION

The results given in Figures 1-6 indicate that the method of the measurement of the work of separating the plies of a laminate is capable of wide application The apparatus used is standard equipment in many textile laboratories and the technique is simple and straightforward

Apparently, the only drawback is the amount of material necessary, especially if the full range of test widths is used However, this increases the value of the result as it is obtained from a greater area of material.

For research work on new laminated fabrics and for work on the development of existing adhesives and processing methods, tests on specimens of several widths are recommended In the tests given above, the plies in 130 to 180 sq in. of fabric were separated. Fewer tests should suffice for quality control work The number of test specimens of each size could be reduced and/or the range of test specimen sizes reduced Alternatively, the construction of a graph could be omitted and the difference in the work required to peel 2 sq in and 1 sq in would give a reading numerically equal to the suggested ballistic peel factor, provided, of course, that the widths of the test specimens in both cases are identical.

The results obtained on materials other than fabric laminates are not intended to serve as comparisons between the respective materials, adherends and adhesives were used because they were to hand and would serve to demonstrate the types of systems that could be tested by the suggested method No claim is made that the method in itself offers a means of completely evaluating an adhesive, but it should prove useful as an additional approach to the far from simple problem of assessing adhesives

ACKNOWLEDGEMENT

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REFERENCES

[1] Hough, W "Cotton Fabrics" pp 30–31.

[2] Haven, G B "Industrial Fabrics" pp 165–176 and pp 177–193 Wellington Sears Co, 1938, New York

[3] A S T M, D 413–39. Adhesion of vulcanised rubber, friction test.

[4] Ellis, C "The Chemistry of Synthetic Resins," p. 1367 Reinhold Publishing Corp., 1935, New York.

[5] Braude, F "Adhesives," Chapter II, pp 4–6 Chemical Publishing Co, 1943, Brooklyn

[6] Bowles, R F "Tack of Printing Ink," *Paint Technology*, 1944, 9, No. 106.

[7] Rivlin, R S "The Effective Work of Adhesion," *Paint Technology*, 1944, 9, No 106.

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Newport (Mon.).

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30—THE INTEGRAL AND DIFFERENTIAL HEATS OF SORPTION OF WATER BY CELLULOSE

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I. INTRODUCTION

Experimental values of heat of wetting or integral heat of sorption, and derived values of the differential heat of sorption of cellulosic fibres are limited in the literature. Shorter[1] showed that it was possible to calculate values of the differential heat of sorption of a fibre, by applying a form of the Kirchoff equation for the heat of dilution to adsorption isotherms at temperatures which were reasonably close together This has been done by various authors, both for cellulose and protein fibres Katz[2] pointed out that direct measurements of the heat of wetting would yield differential heat of sorption values, by measuring the slope of the heat of wetting/moisture regain curve This latter method, sometimes called the direct one, was used in the experiments which are the basis of this paper and the technique is that of Rees[3]

Heat of absorption data for Texas cotton, mercerised cotton, Tenasco and Fortisan have been published by Rees[3] This work is a continuation of that of Rees and the majority of cellulosic fibres have now been studied.

II. THEORY

The method used by Rees[3] and the author is known as the direct or calorimetric method for evaluating integral and differential heats of sorption. The quantity measured experimentally is the integral heat of sorption, or heat of wetting, which is defined as the heat evolved when the material at a given moisture regain C is completely wetted out, and is expressed in calories per gram of the dry material

The differential heat of sorption, or heat of absorption, is the heat evolved when 1 gram of water is absorbed by an infinite mass of material and is expressed in calories per gram of water absorbed.

The integral and differential heats of sorption are related by

$$\Delta H = -100\,\frac{dW}{dc} \quad \ldots \ldots \ldots (1)$$

where ΔH is the differential heat of sorption, W is the integral heat of sorption and c is the moisture regain. In this paper ΔH refers to the sorption of liquid water and not to that of water vapour, and is a common notation.[4,6,9,10,12]

The differential heat of sorption may also be calculated by the indirect or isosteric method which was first used by Shorter[1] By thermodynamic reasoning he deduced an equation which is a form of the Kirchoff equation for heats of dilution and is

$$\Delta H = \mathbf{R}T^2\left(\frac{d\log r}{dT}\right)_c$$

$$\text{or } \Delta H = -\mathbf{R}\,\frac{d\log r}{d(1/T)} \quad \ldots \ldots (2)$$

where T is the absolute temperature, **R** is the gas constant and r the relative humidity.

If a given moisture regain c is maintained by a relative humidity r_1 at temperature T_1 and also by relative humidity r_2 at temperature T_2, and it is assumed that ΔH does not vary appreciably between T_1 and T_2 then equation (2) may be written

$$\Delta H_0 = \frac{\mathbf{R}T_1T_2\,(\log r_2 - \log r_1)}{T_2 - T_1} \quad \ldots \ldots \ldots (3)$$

This equation may be used directly with moisture adsorption isosteres, obtained by plotting log vapour pressure against $1/T$

Owing to the hysteresis effect, thermodynamics cannot strictly be applied, since the process is not reversible, but various authors[1,5,6,7,8,9,10] have used this method and fair agreement with the calorimetric method has been obtained. Rees[3] has commented on limitations to the accuracy which may be obtained.

When the differential heat of sorption has been evaluated the entropy change may be calculated A thermodynamic treatment of sorption and swelling, analagous to that applied to dilute solutions was put forward by Katz [2] Valko,[4] Babbitt[5] and White and Eyring[6] have reviewed the position. The general expression for the free energy of a system at constant pressure and temperature is

$$\Delta F = \Delta H - T.\Delta S \quad \ldots \quad (4)$$

ΔF is the decrease in free energy occurring when 1 grame of water is added to an infinite mass of cellulose under given conditions, and ΔS is the net entropy decrease in excess of the entropy of condensation of water vapour to liquid water.

In the swelling process $p.\Delta V$ (ΔV is the volume change) may be neglected compared with the work done and hence the latter may be equated to the free energy change The change in the work function of 1 g of water vapour, treated as a perfect gas is $\frac{\mathbf{R}T}{M}\log_e\frac{p_s}{p}$ where p is the equilibrium vapour pressure of the cellulose/water system, p_s the saturation vapour pressure, and M the molecular weight of water vapour

Equation (4) may now be written

$$\frac{\mathbf{R}T}{M}\log_e\frac{p_s}{p}=\Delta H-T.\Delta S \quad . \quad . \ ... \ . \ . \ ... \ .(5)$$

Values of $\frac{\mathbf{R}T}{M}\log_e\frac{p_s}{p}$ may be calculated, ΔH is derived from experimental data and so ΔS may be evaluated.

At equilibrium pressures approaching zero, $\frac{\mathbf{R}T}{M}\log_e\frac{p_s}{p}$ will approach infinity, implying that ΔH or ΔS also approaches infinity. Rees[3] and the author have obtained finite values of ΔH for both dry samples and samples of small moisture regain. Neale and Stringfellow[7] working at extremely low relative humidities also obtained finite values for the differential heat of sorption. Hence it appears reasonable to apply equation (5) except at relative humidities approaching zero.

III. A SUMMARY OF PREVIOUS WORK

Rees[3] has summarised literature concerning the integral and differential heats of sorption of textile fibres. Several additional points of interest will now be briefly mentioned.

Razouk[11] has given a critical review of various theories of the heat of wetting, and of methods for its measurement. Katz[2] compared the decrease of free energy with the differential heat of swelling which showed that something more was occurring than the force of attraction between solid and liquid Either the degree of association of the water is changed through the swelling, or some regular arrangement occurs as in the formation of crystals Stamm and Loughborough[9] (wood) and Houtz and MacLean[10] (paper) calculated differential heats of sorption from adsorption isotherms and their results for Δs were in fair agreement. Simril and Sherman Smith[12] showed that the differential heat of sorption is not independent of temperature. The moisture hysteresis loop is interpreted on the basis of the entropy of the sorbed water, and the resulting theory is an extension of that of Urquhart.[13] Babbitt[5] summarised data from several sources and Brunauer[15] has given a detailed account of the theoretical aspects of heat of adsorption.

IV. APPARATUS AND EXPERIMENTAL TECHNIQUE

The calorimeters and experimental procedure have been described by Rees.[3] Briefly, a sample which has been carefully conditioned is released from its sealed container under water in a Dewar flask, and the temperature rise is noted by means of a series of thermocouples. A second flask provides the constant-temperature thermojunction, the whole apparatus being enclosed in an air thermostat at 25° C. The second part of the experiment consists of heating the flask and sample by a known electric current so as to obtain approximately the same temperature rise. Galvanometer deflections are corrected for loss by cooling and the integral heat of sorption is obtained from:—

$$W=\frac{I.V.t.d_1}{4{\cdot}18.w.d_2} \quad . \quad . \ .. \quad . \ .. \qquad (6)$$

where V is the potential drop across the heating coil in volts, t is the time in seconds that current I amps. passes through the heating coil, w grams is the dry weight of the sample, and d_1 and d_2 are the corrected galvanometer deflections for the wetting and electrical heating parts of the experiment.

The estimated experimental error gives an accuracy of ±0·5 per cent.

Materials Used and Their Preparatory Treatments

(*a*) Bengals cotton and Montserrat Sea Island cotton, both yarns of 10s count and twist factor 2·5, were given the following sequence of treatments: ments:

(i) Scour, 3 hours, 1 per cent. NaOH+0·15 castor oil soap at 30 lb. pressure.
(ii) Scour, 3 hours, 1 per cent. NaOH only
(iii) Bleach, ½ hour, N/25 sodium hypochlorite, *pH* 11.
(iv) Sour, N/10 hydrochloric acid, ½ hour, and washed free from acid with distilled water.

(*b*) Flax:—Yarn fully boiled and bleached.

(*c*) Rayons:—All in yarn form

Viscose	150 den./27 fil.	Soured, washed free from acid with distilled water and extracted with ether
Spun viscose	6s	
Spun viscose	10s	
High-tenacity viscose (Durafil)	30/100	
High-tenacity viscose (Tenasco 20%, 40%, 60%, 80% stretch)		
Cuprammonium	150/112	

Cellulose acetate (Seraceta) 250/48; Extracted with ether.

Conditioning

After the above treatments all samples were conditioned from the dry state, and great care was taken over the conditioning process. Samples were first placed over phosphorus pentoxide in a vacuum desiccator for at least three weeks. Samples for measurements at zero regain were quickly transferred to the glass container and sealed off by the aluminium stopper. These were then evacuated through phosphorus pentoxide tubes by a mercury diffusion pump backed by a Metrovac rotary oil pump. It was found by weighing at intervals that samples were perfectly dry after three days on the pumps. It was possible to dry four samples at once.

Conditioning to regains other than zero was carried out both by the method described by Rees, and also by storing over sulphuric acid solutions in desiccators. The relative humidities corresponding to the strengths of the sulphuric acid solutions were obtained from tables by Wilson.[16]

All conditioning was carried out at 25° C. and in every experiment the moisture regain of the sample was determined. The conditioned sample was weighed before wetting out and its dry weight obtained by heating for 16 hours at 106° C. in a drying oven. When dry samples were wetted out there was no significant difference between the weights after drying over phosphorus pentoxide prior to the experiment and the oven dry weights measured afterwards

V. EXPERIMENTAL RESULTS AND DISCUSSION

Integral heat of sorption measurements were made on the materials listed above and the results are shown in Table I (see Appendix)

Curves have been drawn of integral heat of sorption plotted against moisture regain, and are shown in Figs. 1 and 6.

All measurements were made on samples which had been conditioned from zero regain to their final value, *i.e.* their moisture regains all fall on the main adsorption curve. No experiments were carried out on samples conditioned by desorption and no information was obtained on the effect of hysteresis. Argue and Maass[25] showed that the integral heat of sorption of a sample conditioned by desorption was greater than the value obtained after conditioning by adsorption to the same moisture regain.

Differential Heat of Sorption

(*a*) *Calorimetric method.* From the curves obtained by plotting the integral heat of sorption against moisture regain values of the differential heat of sorption were derived using equation (1). The slopes of the curves were measured with a slope meter and in the vicinity of zero regain by calculation from a fitted polynomial Differential heats of sorption are listed against moisture regain in Table II (see Appendix).

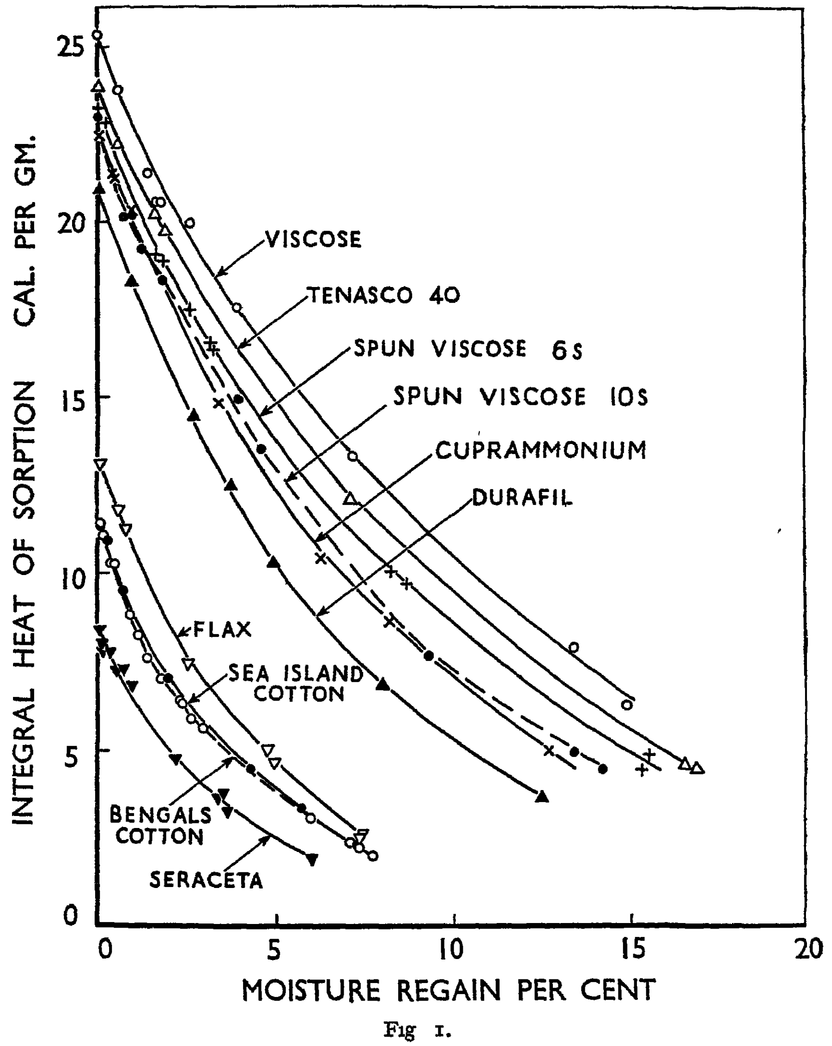

Fig 1.

The values of ΔH for the various dry fibres lie on either side of a mean value of 297 cal./g of water absorbed. Hermans[17] has stated that if the average constitution of the amorphous parts of all cellulosic materials is approximately the same, then the intensity factor of sorption should be the same for all the materials This requires that the differential heats of sorption at zero moisture regain are equal.

The figures of Table II do not rigidly prove this, but they do indicate that the conclusion is probably correct. Neale and Stringfellow[7] calculated ΔH by the isosteric method, from accurate moisture regain measurements on cotton at very low humidities, and obtained a value of 289 cal./gram. Values of ΔH at zero regain by other authors vary considerably, the figures falling between approximately 200 cal /g., for cotton by Strachan[18] (an extrapolated value) to 387 cal./g. by Babbitt[5] from data by Katz on cellulose. Simril and Sherman Smith[12] quote the upper value to be 800-1,000 cal./g. of water. The values of Rees (average 283 cal./g.) and the author for the differential heat of sorption at zero regain may be said to be approximately equal. The differences appear at first sight to be too large to come under the classification of experimental error. However, the slopes of the integral heat of sorption curves are greatest at zero moisture regain and a very small difference in the measured value of W or moisture regain will have a very large effect on the value of ΔH.

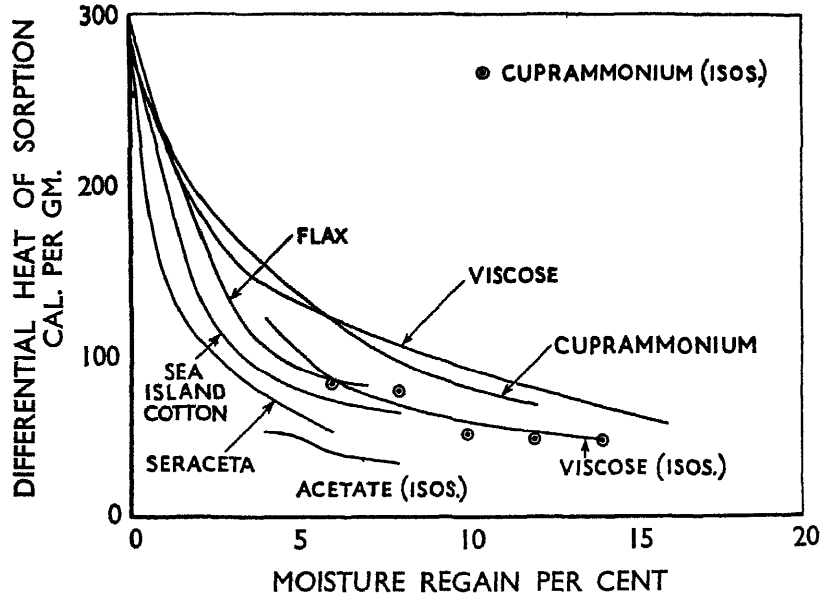

Fig. 2.

For the present it will be sufficient to regard the values as approximately equal and that the nature of the absorbing material of all cellulosic materials is approximately the same. The values of the integral heats of sorption at zero regain will therefore indicate the relative amounts of absorbing material present in the different fibres, again approximately.

Curves of the differential heats of sorption of viscose rayon, cuprammonium rayon, flax, Sea Island cotton and Seraceta plotted against moisture regain are shown in Fig. 2. Curves of other fibres are omitted for the sake of clearness. With increasing moisture regain from zero the value of ΔH falls off rapidly at first, and in the region of moisture regains corresponding to normal room relative humidities the curves flatten out appreciably.

(*b*) *Isosteric method.* Calculated values of the differential heat of sorption of viscose, cuprammonium and acetate rayons were obtained by the isosteric method from moisture adsorption isotherms by Wiegerink,[19] whose data applied to the range of temperatures 96-302° F. Absorption isosteres were drawn and the straight lines extended to 68° F. Values of ΔH were then calculated by means of equation (3), and are shown in Fig. 2.

These isosteric values are less than the calorimetric values of Table II by amounts of the order of 40 cal /g. at 6 per cent. moisture regain, decreasing to about 23 cal./g at 12 per cent. moisture regain for viscose and cuprammonium Values for acetate rayon are less by 22 cal /g. at 4 per cent. moisture regain, decreasing to 11 cal /g at 6 per cent. moisture regain when referred to Seraceta values in Table II.

Hermans[20] has commented that values of the differential heat of sorption by the isosteric method are always less than values by the direct method. This is supported by the above results. It is a debatable point as to which values of moisture regain should be used for thermodynamic calculations, as in the isosteric calculation of differential heat of sorption. Most calculations have been carried out on adsorption values chiefly because, with the exception of the data of Wiegerink,[19] the temperature effect on sorption was usually measured for adsorption isotherms only. The correct value thermodynamically may be on a curve intermediate between the main adsorption and desorption curves. In this paper the isosteric calculations were made on points on the main adsorption curve.

Deductions from Values of Integral Heats of Sorption

The integral heat of sorption data yield information regarding the relative amounts of water binding material in the different fibres. Rees[3] has commented on values at zero moisture regain, and for regains other than zero Hermans[21] derived corresponding moisture regains for cotton and viscose rayon, which he compared with the moisture sorption ratios.

The hypothesis that the absorbing material of all cellulosic fibres is the same in average constitution may now be tested in two ways.

First, the co-ordinates of points on the curves of Fig. 1 should differ in scale only. That is, by applying a ratio to both co-ordinates of all points on the curve for say viscose rayon, it should be possible to cause the curve to coincide with that of, say, Sea Island cotton. Fig. 3 shows experimental points, for all the fibres on which measurements were made, which have had their co-ordinates reduced, with Sea Island cotton taken as the reference It is clear that all the points lie near to a single curve and that the hypothesis is supported.

The ratios which were applied to the experimental plots for each fibre were obtained as follows. Referring to Fig. 1 lines were drawn from O to A, B and C (chosen arbitrarily), and the distance of each curve from O was measured along OY, OA, OB and OC. The ratios of the distance of each curve from O to the distance of the curve for Sea Island cotton from O was calculated, and an average value obtained for each material from the four directions OY, OA, OB and OC. These average ratios were then used to reduce the co-ordinates of the axes of experimental points to those of Sea Island cotton.

The values of the average integral heat of sorption ratios are shown in Table III (see Appendix)

The second test is to compare these values with the average values of moisture sorption ratios of Urquhart and Eckersall[22] which are shown in the last column of Table III The agreement is fair only. The values for viscose, cuprammonium, spun viscose 10s and Seraceta are in accordance with an observation of Hermans and Weidinger[23] that integral heat of sorption ratios are generally higher than moisture sorption ratios

Differential Heat of Sorption and Relative Humidity

Babbitt[5] pointed out the advantage of plotting the differential heat of sorption against relative humidity instead of moisture regain. If the average constitution of the water absorbing regions of all cellulosic fibres is the same it follows that the differential heat of sorption/relative humidity curves should be the same for all fibres.

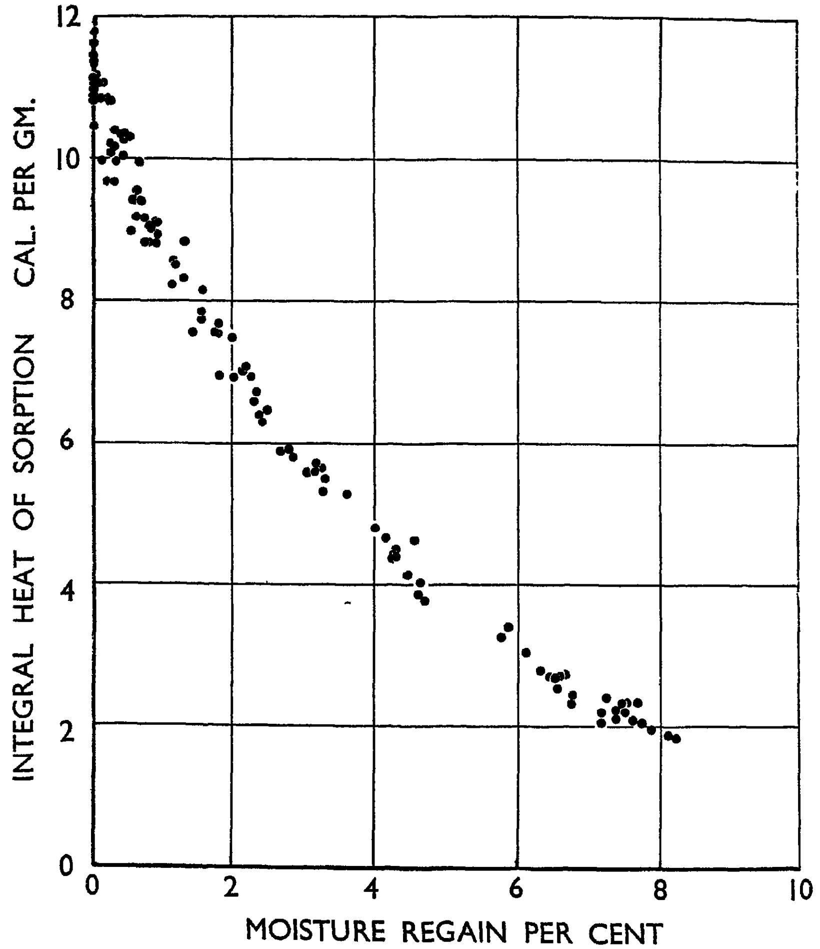

Fig 3

In Table IV (see Appendix) values of the differential heats of sorption of different cellulosic fibres are shown against values of relative humidity Use was made of moisture absorption isotherms for the three cottons by Urquhart and Williams,[24] and for the rayons by Urquhart and Eckersall.[22] The samples of spun viscose were found to have moisture regains very near to those of the latter authors for Fibro. The differential heat of sorption data are by the present author except for Texas cotton, cotton mercerised without tension, and Tenasco, which are by Rees.[3]

Table IV shows that for a given relative humidity the values for the differential heats of sorption of the various fibres agree fairly well although there are admittedly quite large deviations. The values when plotted against relative humidity fall within an area or loop as shown in Fig 4.

Continuing with the concept that all cellulosic materials are identical regarding the nature of the process of water sorption and differ only in the numbers of active groups available, it was considered advantageous to draw a single curve for ΔH against relative humidity. This curve is an approximation and is taken to represent the variation of the differential heat of sorption of cellulose with relative humidity. It is shown in Fig. 5 together with a curve by Babbitt[5] which he obtained from the results of other authors, all of whom except Argue and Maass used the isosteric method. Babbitt's curve falls below that of the author and is another instance of values of differential heats of sorption obtained by the isosteric method being less than those obtained by the calorimetric method

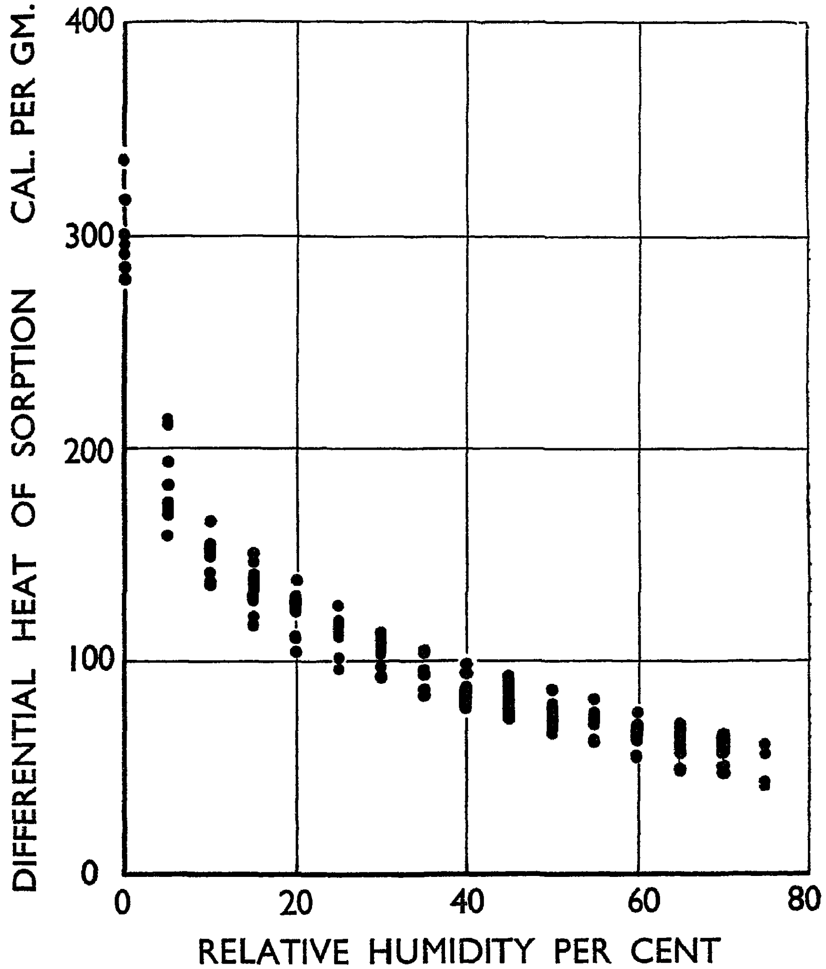

Fig 4

Values of ΔH decrease rapidly with increasing relative humidity at low humidities and after about 15 per cent relative humidity the slope is fairly uniform and of a much smaller value than initially. Values were not obtained for humidities above 70 per cent, but it would appear that ΔH will have a very small value near saturation. In this region the free energy approaches zero and ΔS will also be very small. This means that water absorbed near saturation will be very similar to liquid water. The steep slope of the curve as zero regain is approached shows that very strong forces must be operating during the initial stages of water sorption, and these have been discussed by Neale and Stringfellow.[7]

Differential heat of sorption values for jute have been obtained by MacMillan, Mukherjee and Sen[26] by the isosteric method. Values of differential heat of sorption for given relative humidities were derived which are lower than the average values of ΔH as shown in Fig. 5. At 25 per cent. relative humidity the values are nearest to those of Bengals cotton. The above authors state that the presence of lignin, xylan and other hemicelluloses in jute may modify its moisture absorption properties

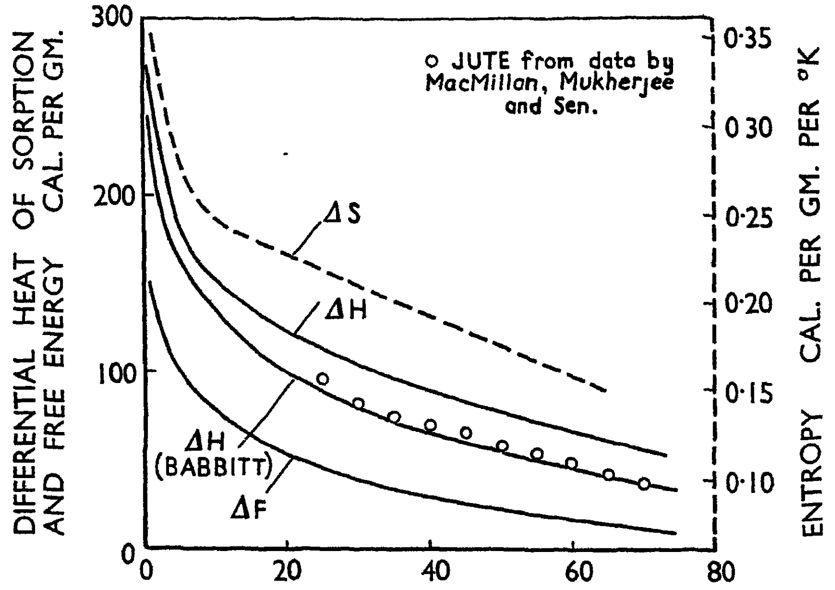

Fig 5

Free Energy and Entropy

Free energy values $\left(\frac{RT}{M}\log_e\frac{p_s}{p}\right)$ were calculated and from equation (5) values of $T\,\Delta S$ and ΔS were obtained by using ΔH values from the curve of Fig. 5. Free energy (ΔF) and entropy (ΔS) values are plotted in Fig 5 from the data of Table V.

The entropy values being average ones are approximate only. It is noteworthy, however, that Stamm and Loughborough quote 0·34 for the entropy change of spruce wood with a value of ΔH of 270 cal./gm. Their corresponding figures for cotton calculated from data by Urquhart and Williams are 0·26 and 280 cal /gm , respectively

$T.\Delta S$ values represent the excess energy held by the sorbed water and a value of 105 cal /gm. was obtained at 1 per cent. relative humidity. Babbitt's[5] value is 81·6 cal /gm The latter author also used the moisture sorption data on cotton of Urquhart and Williams[27] to calculate E_1-E_2 in the theory of Brunauer, Emmett and Teller[14] and obtained a value of 89·5 cal./gm.

Effect of Stretching on High-tenacity Viscose Rayon (Tenasco)

The values of the integral heats of sorption of the four samples of Tenasco (Table I and Fig. 6) decrease as the percentage stretch is increased; *e g.*, at zero moisture regain the integral heats of sorption for 20, 40, 60 and 80 per cent. stretch are 24·5, 23·8, 23·3 and 22·7 cal./gm., respectively. Thus, as Tenasco is stretched the amount of water-absorbing material decreases. That its nature does not change is shown by the differential heat of sorption values (Table II) which are approximately the same for all four samples, except in the region below 1 per cent. moisture regain where there are appreciable differences The conclusion may therefore be drawn that stretching, which increases the orientation of the chain molecules, causes a slight decrease in the hygroscopicity of the fibre.

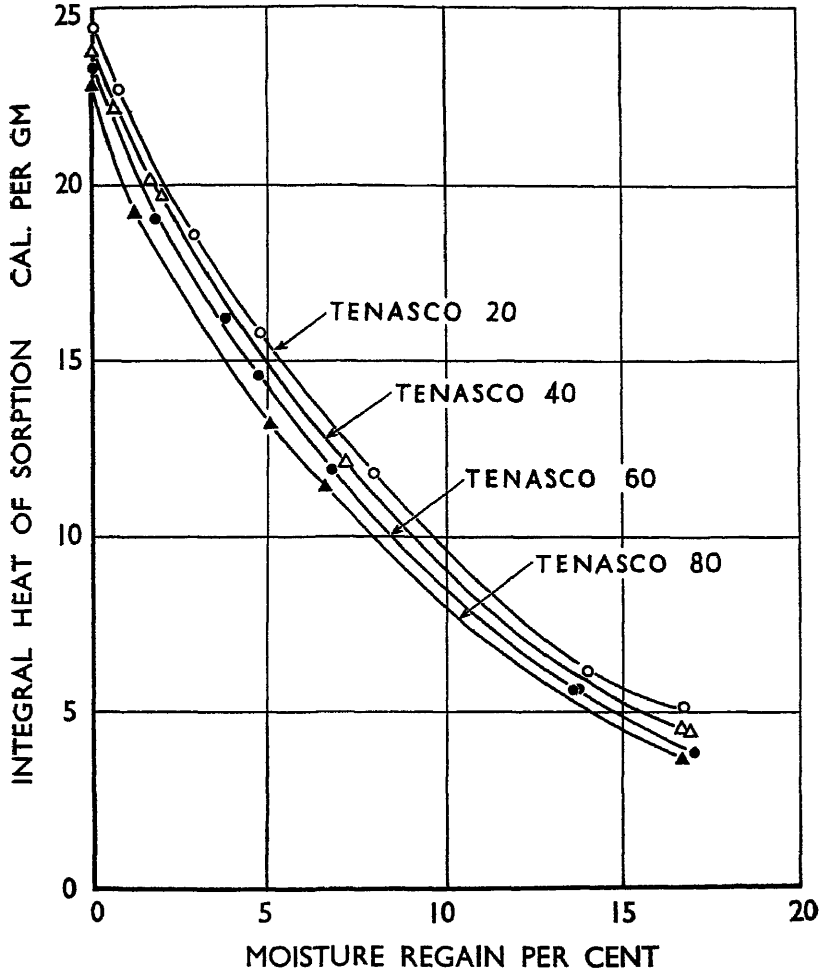

Fig 6

This is borne out by the values of moisture regains determined at 25° C. and 65 per cent. relative humidity Tenasco, 20, 40, 60 and 80 per cent. stretch, had, respectively, moisture regains of 15·4, 14 9, 14·5 and 13·8 per cent.

VI. SUMMARY

Previous work by Rees has been extended and integral and differential heats of sorption of most cellulosic fibres have now been evaluated Additional references to the literature, which mainly concern the evaluation of thermodynamic functions, are given.

Differential heats of sorption at zero moisture regain are approximately equal for all cellulosic fibres, the average value being 297 cal./gm. of water absorbed. This supports the hypothesis that the average constitution of the water-absorbing regions of cellulosic material is the same for all.

Also supporting it, is the fact that when integral heats of sorption are plotted against moisture regain on "reduced co-ordinates", the values all fall near a single curve. Comparison between integral heat of sorption ratios and moisture sorption ratios for five fibres shows only fair agreement.

Differential heats of sorption when plotted against relative humidity may be represented by a single curve which is approximately correct. At 1 per cent. relative humidity the approximate value of the change of entropy is 0·35 cal /gm.° absolute for cellulosic materials

Samples of high-tenacity viscose rayon (Tenasco) which had been stretched by different amounts showed a decrease in the value of integral heat of sorption with increasing percentage stretch, indicating a decrease in hygroscopicity with stretching.

REFERENCES

[1] Shorter, S A. *J. Text Inst*, 1924, 15, T328.
[2] Katz, J R. *Trans Faraday Soc*, 1933, 29, 279.
[3] Rees, W H *Shirley Inst Memoirs*, 1947, 21, 333, or *J. Text Inst*, 1948, 39, T351.
[4] Valko, E I "Cellulose and Cellulose Derivatives," edited by Emil Ott, Interscience Publishers, 1943, page 394
[5] Babbitt, J. D *Canadian J. Res*, 1942, 20A, 143
[6] White, H J, and Eyring, H *Textile Research J.*, 1947, 17, 533.
[7] Neale, S M, and Stringfellow, W A *Trans Faraday Soc*, 1941, 37, 525
[8] Newsome, P T, and Sheppard, S E *J Phys Chem*, 1932, 36, 930.
[9] Stamm, A J, and Loughborough, W. K *J Phys Chem*, 1935, 39, 121.
[10] Houtz, C C, and MacLean, D A *J Phys Chem*, 1941, 45, 111
[11] Razouk, R I *J Phys Chem*, 1941, 45, 179 and 190
[12] Simril, V L, and Smith, S *J Ind Eng Chem*, 1942, 34, 226.
[13] Urquhart, A R. *Shirley Inst. Memoirs*, 1929, 8, 27, or *J Text Inst*, 1929, 20, T125.
[14] Brunauer, S, Emmett, P H, and Teller, E *J. Amer Chem Soc*, 1938, 60, 309
[15] Brunauer, S "Physical Adsorption of Gases and Vapours," Oxford University Press, Chapters VII and VIII
[16] Wilson, R E *J. Ind Eng Chem*, 1921, 13, 326.
[17] Hermans, P H "Contribution to the Physics of Cellulose Fibres" Elsevier, 1946, p 11
[18] Strachan, E K *Amer Dyes Rep*, 1938, 27, 240.
[19] Wiegerink, J. K *Textile Research J*, 1939-40, 10, 357
[20] Hermans, P. H *Loc. cit*, p 41
[21] Hermans, P H *Loc cit*, p 39
[22] Urquhart, A R, and Eckersall, N *Shirley Inst Memoirs*, 1932, 11, 75, or *J Text. Inst*, 1932, 23, T163
[23] Hermans, P H, and Weidinger, A. *J Amer Chem Soc*, 1946, 68, 2551
[24] Urquhart, A. R, and Williams, A M. *Shirley Inst Memoirs*, 1925, 4, 167, or *J. Text. Inst*, 1925, 16, T155
[25] Argue, G H, and Maass, O *Canadian J. Res*, 1935, 12, 564
[26] MacMillan, W G, Mukherjee, R R, and Sen, M K *J. Text Inst*, 1946, 37, T13
[27] Urquhart, A R, and Williams, A M *Shirley Inst Memoirs*, 1924, 3, 197, or *J. Text. Inst*, 1924, 15, T559

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APPENDIX

Table I

Experimental Values of the Integral Heat of Sorption of Some Cellulosic Fibres

Moisture regain %	W, cal./gm., dry material
Cotton, Bengals	
0	11·3
0·11	10·9
0·31	10·3
0·41	10·2
0·86	8·70
1·09	8·12
1·37	7·46
1·73	6·87
2·29	6·28
2·33	6·19
2·59	5·79
2·95	5·50
5·99	2·97
7·09	2·35
7·35	2·13
7·71	1·90
Cotton, Sea Island	
0	11·2
0·24	10·8
0·67	9·37
1·95	6·90
4·24	4·37
5·70	3·23
7·30	2·20
Flax	
0	13·0
0·51	11·6
0·73	11·2
2·50	7·34
4·71	4·91
4·93	4·59
7·38	2·45
7·47	2·55
Viscose rayon	
0	25·2
0·6	23·6
1·4	21·3
1·65	20·4
1·81	20·4
2·63	19·8
3·95	17·5
7·19	13·2
13·45	7·8
14·95	6·15

Moisture regain %	W, cal/gm., dry material
Spun viscose 6s	
0	23·2
0·26	22·8
1·65	18·9
1·85	18·7
3·15	16·4
3·20	16·2
8·27	9·9
8·58	9·7
15·33	4·39
15·53	4·82
Spun viscose 10s	
0	22·9
0·69	20·0
0·86	20·1
1·22	19·1
1·83	18·3
3·92	14·9
4·58	13·4
9·32	7·53
13·45	4·85
14·26	4·36
Durafil	
0	20·8
0·93	18·2
2·7	14·3
3·69	12·4
4·92	10·2
8·04	6·76
12·54	3·54
Tenasco, 20% stretch	
0	24·5
0·71	22·6
2·84	18·5
4·77	15·7
7·90	11·7
13·95	6·14
16·7	5·08
Tenasco, 40% stretch	
0	23·8
0·54	22·1
1·61	20·1
1·95	19·6
7·10	12·0
16·6	4·5
16·88	4·4

Moisture regain %	W, cal.gm., dry material
Tenasco, 60% stretch	
0	23·3
1·73	19·0
3·7	16·1
4·64	14·5
6·7	11·8
13·49	5·6
13·63	5·7
16·95	3·85
Tenasco, 80% stretch	
0	22·7
1·17	19·2
4·95	13·1
6·50	11·3
16·63	3·65
Cuprammonium rayon	
0	22·4
0·4	21·2
0·45	21·2
0·85	20·2
2·5	17·3
3·4	14·7
6·29	10·4
8·19	8·55
12·71	4·96
Seraceta	
0	8·24
0·08	7·86
0·15	7·63
0·22	7·63
0·4	7·09
0·67	7·17
0·9	6·71
2·15	4·65
3·33	3·5
3·55	3·64
3·60	3·15
5·99	1·82

Table II Differential Heat of Sorption—Derived Results

Moisture regain %	Differential Heat of Sorption—Calories per gram of water absorbed												
	Bengals cotton	Sea Island cotton	Flax	Viscose	Spun viscose 6s	Spun viscose 10s	Durafil	Tenasco				Cuprammonium	Seraceta
								20% Stretch	40% Stretch	60% Stretch	80% Stretch		
0	317	295	298	280	290	335	296	272	279	290	330	290	295
0·5	297	261	253	255	259	290	273	229	223	254	280	263	200
1·0	223	213	232	229	239	210	246	220	204	234	255	228	145
1·5	168	160	206	205	220	197	218	202	190	195	192	216	120
2	135	138	185	190	188	185	204	189	185	182	172	209	94
3	101	111	123	151	146	163	200	154	160	157	155	174	87
4	87	83	98	138	132	154	154	139	140	135	134	154	73
5	72	77	88	127	128	134	137	133	134	138	130	139	64
6	64	71	83	120	116	125	111	129	123	122	120	118	49
7	59	67	80	109	106	118	102	120	118	120	112	107	—
8	58	64	—	104	103	108	91	112	116	113	110	89	—
10	—	—	—	93	87	87	74	91	90	93	81	79	—
12	—	—	—	74	73	61	65	82	74	73	68	68	—
14	—	—	—	64	60	48	—	57	59	57	58	—	—
16	—	—	—	54	54	—	—	53	45	52	51	—	—

Table III Comparison of Integral Heat of Sorption Ratios with Moisture Sorption Ratios

Fibre	Integral heat of sorption ratio	Moisture sorption ratio	Fibre	Integral heat of sorption ratio	Moisture sorption ratio
Seraceta	0·79	0·7 (approx.)	Spun viscose, 6s	2·1	—
Bengals cotton	0·99	—	Viscose	2·32	1·9
Flax	1·12	—	Tenasco, 20% stretch	2·23	—
Durafil	1·77	1·93	„ 40% „	2·2	—
Cuprammonium	1·96	1·87	„ 60% „	2·11	—
Spun viscose, 10s	2·01	1·81	„ 80% „	2·04	—

Table IV
Variation of the Differential Heat of Sorption of Cellulosic Fibres with Relative Humidity

Relative humidity %	Differential Heat of Sorption, Calories per gram of water absorbed											
	Bengals cotton	Sea Island cotton	Viscose	Spun viscose 6s	Spun viscose 10s	Durafil	Cuprammonium	Tenasco 40% Stretch	Seraceta	*Texas cotton	*Tenasco	*Cotton Mercerised W T
0	317	295	280	290	335	296	290	279	295	285	291	280
5	175	172	167	158	173	169	171	168	214	210	182	194
10	135	137	141	140	154	154	149	147	161	149	164	164
15	116	120	130	128	140	136	133	133	133	130	150	146
20	105	110	122	121	128	122	122	125	111	123	137	130
25	97	102	115	114	119	112	112	117	99	115	125	118
30	90	93	109	107	109	97	103	111	90	103	113	105
35	84	87	104	101	102	94	93	104	83	95	104	95
40	79	82	98	93	93	86	88	96	77	85	94	86
45	74	77	92	87	85	80	83	90	73	77	85	78
50	68	74	87	80	77	75	78	82	67	70	75	69
55	65	72	82	75	70	71	72	73	62	64	66	63
60	63	70	76	69	63	66	68	64	57	55	57	55
65	60	67	71	64	56	63	64	58	53	48	52	50
70	57	65	64	59	49	—	61	52	—	—	47	—
75	—	—	58	55	40	—	57	—	—	—	47	—

*Heat data by Rees.

Table V

Changes in the Differential Heat of Sorption, Free Energy, and Entropy of Cellulosic Fibres, with Relative Humidity

Relative humidity %	ΔH, cal./g	ΔF, cal /g	$T.\Delta S$, cal./g.	ΔS, cal./g./° T
1	256	151·0	105 0	0·35
2	229	128 2	100·8	0 34
5	178	98·5	79 5	0·27
10	150	76 6	73·4	0·25
15	133	63·0	70·0	0·24
20	121	53 5	67 5	0·23
25	111	46 1	64 9	0·22
30	103	40 0	63 0	0·21
35	96	34 9	61·1	0·20
40	88	30 4	57·6	0·19
45	82	26·6	55 4	0 19
50	75	23 0	52·0	0 18
55	69	19·9	49·1	0·17
60	63	17·1	45·9	0 15
65	59	14 3	44·7	0·15
70	57	11·9	45·1	0·15
75	50	9·5	40·5	0·14

31—A STUDY OF THE EFFECTS OF LAUNDERING AND STORAGE ON COTTON CLOTH*

By MARY E. MURDISON† and JESSIE S. ROBERTS‡

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INTRODUCTION

The fundamental changes occurring in cotton fabric during wear are as yet unknown. This study was undertaken to determine by means of microscopical, chemical, and physical tests some of the changes which had taken place in cottons laundered up to 100 times Variations in tensile strength and fluidity in cuprammonium were recorded after repeated launderings, and a microscopical technique using Congo Red after the method of Clegg[4] was employed to reveal wear as it was registered in damage to the fibre. The majority of the cotton samples for the test had been put through the laundering processes in 1940. At this time, extent of degradation had been estimated by tensile strength loss and increase in fluidity only. In the present study, tensile strength and fluidity determinations were repeated, and in addition the Congo Red test was used For purposes of comparison, a fresh series of cotton fabrics was laundered 100 times, and the same determinations were made. This was necessary to find out whether any of the visible tendering had been due to the eight years ageing

The visible reactions of the cell wall of the cotton fibre are governed by its structure. The primary wall is considered to be composed of a single net-like layer of cellulose, in which the fibrils show three systems of orientation, one transverse to the fibre axis, and two wound spirally at an angle of less than 70° to the main axis.[1,2] The first layer of the secondary cellulose, deposited when the fibre has ceased to grow in length, has been designated by Hock, Ramsay, and Harris as the "winding".[5] It is composed of slightly coarser fibrils, with a moderately steep spiral direction which reverses many times. Beneath this layer lie concentric lamellæ of finer threads, these wind at an acute angle to the fibre axis, forming with the winding the secondary thickening of the cell wall The layer adjacent to the lumen or central canal has been observed by Berkley as distinct from the lamellæ of the secondary wall.[3]

Rupture of the fibre wall during swelling, an integral part of the staining test used in this investigation, has been related to the direction of the cellulose fibrils. Kerr noted that the winding of the secondary cellulose broke invariably parallel to the direction of its cellulose chains, but found that the primary membrane would tear in various ways, often parallel to the orientation of the winding, or to the striations of the main layer.[6] Rollins produced marked spiral patterns in air-dried, mature cotton fibres which were treated with gaseous NO_2, swollen and stained.[7] Clegg demonstrated the tendency of the cuticle to split in a spiral line in the microscopical examination of damaged cotton fibres swollen in NaOH and stained with Congo Red [4]

In this examination, use of the microscopical technique of the Congo Red test demonstrated a qualitative correlation between degrees of visible damage resulting from wear in laundering, and levels of chemical or physical tendering which were shown by loss in tensile strength and increase in fluidity.

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EXPERIMENTAL

Procedure—Order of Examination

A preliminary study of several series of fibres from identified sources was made. These were chosen to illustrate the specific effects of individual wear factors which would be met in the laundered cloths under examination. The results of storing raw cotton were investigated on samples of year crops back to 1935 obtained from the United States Department of Agriculture. The effects of processing cotton through spinning, weaving, and finishing were studied on samples obtained directly from mills The appearance of raw cotton after storage, and of unused bleached fabric is particularly described in this report as bearing directly on the control samples of the two laundered series; one had been stored eight years and both were bleached material.

Two sets of laundered cloth were then used for study These had been washed 100 times in 1940 in a gyrator machine by a controlled process (Table I), one set had been dried indoors and one outdoors. The material saved from this experiment had been stored in a cardboard box placed in a dark cupboard in the laboratory for the eight years. The conditions would be similar to home storage in a linen cupboard at average Canadian room temperatures (70°-75° F. except for summer increases).

In 1940, tensile strength and fluidity in cuprammonium on 5 test bundles for each series had been determined at levels of 0, 10, 25, 50 and 100 launderings. In the present study, the tensile strength and fluidity determinations were repeated, and in addition microscopical examination following a staining with Congo Red was made.

To further the investigation, a fresh series was laundered 100 times. An automatic washing machine, not available for use in 1940, was employed to save time. Concentration of soap and dry weight of load were the same as for the 1940 study. (Table II.) Standard cotton fabric, the same as that used in 1940, was obtained through the National Research Council, Ottawa This cloth, which is used in laundry test bundles, is as nearly as possible constant in quality, it is a 36 in fabric, free from sizing, woven with 100 picks and ends per inch A single length of fabric was used for this series, 48 in being cut off for testing as each level of 10, 25, 50 and 100 launderings was reached

Table I
Laundering Process for Gyrator Machine with Wringer
Series Laundered 1940

Process	Equipment Used	Supplies	Time Min	Temp °C.
Soak	Porcelain Laundry Tub	Water 9 Gal	10 approx.	32
Suds	Gyrator Machine	Water 12·5 Gal Na_2CO_3 7·5 Gm * Soap 175 Gm.†	8 exact	67
Rinse	Tub	Water 9 Gal	10 approx.	32
Rinse	Machine	Water 12·5 Gal	8	67
Rinse	Tub	Water 9 Gal	Dipped 3 ×	Cool
Rinse	Tub	Water 9 Gal Blue 3 4 Gm.	Dipped 3 ×	Cold

A steam drier was used for indoor drying, but no record kept of drying times or temperature. Outdoor drying was done on the roof of the Household Science Building.
Load —Clothes were added to keep the load constant at 7 lb. dry wt
Soap.—One lot of pure soap, Colgate Palmolive Peet Golden XXX was used for the entire study

A Coffield gyrator machine with wringer was used.

* Sufficient Na_2CO_3 to soften Toronto water

† Soap to make a 0·3% solution

Table II
Laundering Process for Automatic Machine
Series Laundered 1948

Process	Equipment Used	Supplies	Time Min.	Temp. °C.
Soak	Automatic Machine	Water 5 Gal Capacity	13½	43
Suds	,, ,,	Water 5 Gal. Na_2CO_3 3·3 Gm Soap 75 Gm	16½	67
Flush Rinse	,, ,,	Water	2¼	43
Deep Rinse	,, ,,	,,	6¾	43
Deep Rinse	,, ,,	,,	6	43
Spin Damp Dry	,, ,,	,,	4½	
Dry	Steam Drier		av. 30	55–60

Load, brand of soap, and concentration of soap same as for Series 1940.
A Bendix automatic washing machine was used.

Methods of Testing

(a) *Congo Red Test*

A differential staining of the cotton fibre by Congo Red is the basis of Clegg's microscopical test. After a preliminary swelling in NaOH and a given staining period at room temperature, the intact cuticle* of the fibre takes on a uniform pale pink. In the event of rupture of the cuticle, any cellulose exposed beneath takes up the stain more rapidly, to give a bright red colouring The choice of concentration of caustic for the treatment before staining is based on a study of the swelling of the fibres.[4] If the cuticle is already ruptured by mechanical damage, a 9 per cent. solution of NaOH is sufficient to cause the fibre wall to swell inwardly, but no pressure on the cuticle results. At a concentration of 11 per cent., pressure is exerted outwards on the cuticle; this concentration is used in examination of fibres whose cuticle may be weakened, but not actually torn, for example as a result of heat, light, mildew, or chemical attack. If little or no damage to the fibre is expected, the first immersion is in an 18 per cent. solution of NaOH, which gives maximum swelling pressure.

In this study, a representative sample of fibres was obtained by unravelling 6 in. yarn lengths from eight to ten different areas of the test piece. Before the preliminary swelling, the fibres were dipped in boiling alcohol to ensure thorough wetting. They were given a 3 minute swelling in NaOH at room temperature A concentration of 18 per cent. NaOH was used for raw fibres; 11 per cent. NaOH was employed for fibres from processed and laundered samples. The fibres were then thoroughly washed, dried between filter papers, and stained 10 minutes in a 2 per cent. solution of Congo Red. After the stain had been washed off, the fibres were given a final immersion in 18 per cent caustic soda, to accentuate any colour contrast present. They were mounted in the same 18 per cent NaOH for immediate examination under the microscope A seal of glycerin-gelatine solution was used if the slides were to be kept a day or two.

(b) *Tensile Strength*

Tensile strength was determined by the grab method on a Scott tester, following the method of the A S.T M The samples were previously conditioned to 65 per cent. R H and 70° F. The results reported are the averages of ten determinations.

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* The term " cuticle " is used here in reference both to the cuticle proper and to the primary wall [4]

(*c*) *Fluidity in Standard Cuprammonium Solution*

Five fluidity determinations were carried out at each level. The procedure of the Canadian Government Purchasing Standards Committee Schedule of Methods of Testing Textiles (1947) was followed. Warpwise yarns along the full width of the samples were taken for the 1940 series, to duplicate the method outlined for this study. A representative sampling was obtained for the 1948 series by using warp and weft threads from the full width of the material The fluidities of warp and weft threads were tested separately and found to be identical The averages of the five tests are reported here in reciprocal poises.

(*d*) *Statistical Analysis*

An analysis of variance in tensile strength and fluidity results was performed to ascertain the significance of differences in data collected in 1940 and in 1948 "t" values were calculated to test the significance of differences between the means of values obtained for tensile strength and fluidity determinations on the series laundered in 1948, to indicate at what levels significant wear effects could be noted.

Results

The Congo Red test used for preliminary study of raw fibres from year crops back to 1935 showed only occasional spiral lines or uneven darkly staining spots; there was little other distinguishable "damage" from storage. (Plate I, 1). New raw cotton (Plate I, 2) showed no characteristic breaks at all, except at fibre bends or in abnormally thickened fibres which split in a definite, dark spiral line. Bleaching of woven cotton produced a slight breakdown in the fibres, evidenced by a characteristic faint background spiral pattern which was general on the surface of the fibre. (Plate I, 3). This new bleached material also showed the small amount of mechanical damage resulting from processing—(spinning, weaving and finishing) identified in preliminary studies of fibres of known history.

Examination of Series Laundered in 1940

(*a*) *Congo Red Test*

Progressive and complex damage to the cuticle was observed in fibres from the series of laundered and aged cottons. (Plates II, III, VI). The unlaundered control exhibited the faint spiral pattern found in bleached materials, as well as some small darkly staining crack-like spots and less regular spiral lines which were found on the aged samples only, and are not found characteristically on new bleached material. (II, 4; VI, 13). Mechanical damage was seen to increase more rapidly than chemical weakening in samples from 10 to 25 washings (II, 5, III, 6) Spirals appeared in some areas, but cracks, bruises, or small, ragged abrasions were more common. The faint background of spirals seen in the control was still visible After 50 washes (III, 7), the fibres demonstrated marked mechanical damage, as well as increased chemical effects, shown by darker spiral lines in localized areas. This, however, was not evidenced by all fibres at this level, intense damage was seen in a few fibres, while some others showed little more wear than that seen at lower washing levels. Fibres from samples washed 100 times showed characteristic signs of "all-over" deterioration, with many points revealing severe damage of both types (III, 8). Ragged areas of mechanical rupture were most easily descried, but numerous tiny breaks appeared all over the fibres and dark spiral patterns were also visible. (III, 8; VI, 14).

The Congo Red test distinguished no specific effect from outdoor drying in these aged samples A few localized spirals which were seen in the samples dried outdoors might have been the result of the action of sunlight, but the whole appearance of the fibre damage was too involved to allow this conclusion to be accepted for one set only. Such observations were not consistent nor definite enough to necessitate reporting the results for the samples dried outdoors in 1940 separately from those for the samples dried indoors.

(*b*) *Fluidity in Cuprammonium Hydroxide*

The fluidity values obtained in 1940 and in 1948 on samples of the series laundered in 1940 are shown in Table III These are reported in each case as increases in reciprocal poises over the control pieces from the two bolts of material used The original fluidity values of these controls are given in the footnote to Table III. The values obtained in both testings showed chemical damage at each level of 10, 25, 50 and 100 washings, and those obtained in 1948 were higher than the 1940 results. The fluidity values for the series dried outdoors were again consistently higher than those for the series dried indoors An analysis of variance of the values obtained in 1940 and in 1948 pointed to a significant change of fluidity at all washing levels An effect of chemical degradation on the cotton cellulose from the eight year ageing period was thus indicated

Table III
Fluidity Increase (Fluidity minus Control) Reciprocal Poises, 1940 Series, Laundered in Gyrator Machine, Extracted with Wringer.

Number of Washes	Dried Outdoors		Dried Indoors	
	1940 Data	1948 Data	1940 Data	1948 Data
10	2 1	3 4	0 0	1 7
25	3 5	5 8	1 2	2 3
50	7 5	9 6	3 3	5 0
100	12 0	16 0	6 1	9 8
Control	0 0	1 2	Same Control	
Control	0 0	0 8	Same Control	

Fluidity value of unwashed material first bolt 4 6 R P (Samples for Gyrator Wringer Outdoor, × 10, 25, 50, 100 and Gyrator Wringer Indoor × 10, 25)

Fluidity value second bolt of material 6 8 R P (Samples for Gyrator Wringer Indoor × 50, 100)

Each value given in Table III is the mean of five fluidity determinations

(*c*) *Tensile Strength*

The tensile strength results obtained in 1948 and reported in Table IV showed a decrease similar to that recorded in 1940 in the sample washed zero to 100 times eight years previously The samples dried outdoors exhibited a lower tensile strength than those dried indoors, as was found in 1940. Statistical analysis of the data demonstrated a significant decrease in the values obtained in 1948 from those given in 1940 at all washing levels This indicated a lowering of the tensile strength during eight years ageing.

Examination of Series Laundered 1948

(*a*) *Congo Red Test*

The unlaundered control of the series of cottons laundered in 1948 showed the faint spiral pattern characteristic of chemical weakening from bleaching Mechanical damage was slight, and staining was fairly uniform. (I, 3, VI, 15) The outline of the fibres was practically unbroken, and the tips and ends were not injured After 10 washes (IV, 9) the background of fine spirals was still visible. Although the fibre outline was not much altered at this level, there was a noticeable increase in mechanical damage, revealed by small, darkly staining ruptures. Some ends showed weakening, but most ends and tips were normal By 25 washes many fibres showed increased damage, while others were not distinct from those at the lower washing level (IV, 10) Dark spiral lines, indicative of chemical tendering, were noticed in localized areas only, and most mechanical damage was slight. The ends were both normal and damaged At the 50 wash level, the majority of the fibres showed a marked increase in injury (V, 11). The spirals seen were less localized, and mechanical damage tended to show in splotches of more severe rupture than had been found up to this level Most of the fibre ends were tendered, and stained darkly At 100 washes the faint spirals seen at lower washing levels were almost obliterated by the darker lines which appeared with repeated launderings (V, 12, VI, 16) Areas of intense mechanical damage were interspersed with dark spirals, characteristic of chemical damage, and the cuticle was marked with tiny ragged cuts These stained to give a less even outline and a general weakened effect which distinguished fibres from this level The ends for the most part stained darkly

Table IV
Tensile Strength in Lb—Grab Method
Series Laundered 1940 in Gyrator Machine, Extracted with Wringer

Number of Washes		Dried Outdoors		Dried Indoors	
		1940 Data	1948 Data	1940 Data	1948 Data
10	WARP	43 4	35 8	44 2	36 6
	WEFT	47 4	43 7	49 0	43 1
25	WARP	42 0	34 8	43 7	38 0
	WEFT	47 2	38 4	51 3	46 7
50	WARP	41 8	34 7	43 6	36 5
	WEFT	47 3	38 8	51 1	44 0
100	WARP	38 1	32 0	46 4	40 7
	WEFT	42 6	36 7	51 8	45 9

Each value in Table IV is the average of ten determinations

(b) Fluidity in Cuprammonium Hydroxide

The values for fluidity are given in Table V Calculation of the difference between means showed no significant change in fluidity from that of the control until the 100 wash level, where a chemical weakening was indicated by a significant rise in fluidity

(c) Tensile Strength

There was a gradual decrease in tensile strength over the 100 washes from the values obtained for the unlaundered material, and this change was significant at all levels (Table V)

Table V
Series Laundered 1948 in Automatic Machine

Number of Washes	Fluidity Reciprocal Poises	Tensile Strength in lb —Grab Method	
		WARP	WEFT
0	5 4	48 6	61 5
10	6 5	43 2	58 6
25	6 1	38 2	49 2
50	6 5	40 1	54 9
100	8 0	43 0	55 4

Each fluidity value is the average of five determinations Each tensile strength value is the average of ten determinations

DISCUSSION

Eight years ageing of the cotton materials laundered in 1940 produced both mechanical and chemical weakening, this was shown by the significant decrease in tensile strength and increase in fluidity values at the 10, 25, 50 and 100 wash levels in the 1940 samples re-tested in 1948 The increased tendering effected by outdoor drying was still seen in comparison of the results of tensile strength and fluidity tests on samples dried outdoors with those on samples dried indoors, but no differentiation could be made between these sets using the Congo Red test. The progressive deterioration of the material over 100 launderings which was shown in a gradual lowering of tensile strength and increase in fluidity was reflected in the increasing damage seen in the fibres under Congo Red examination.

Cottons laundered 100 times in an automatic machine (1948 series) showed a decrease in tensile strength at 10, 25, 50 and 100 washes, but an increase in fluidity only after 50 washes Fibres stained with Congo Red demonstrated increasing wear from 0 to 100 washings, mechanical weakening being most noticeable, shown by darkly staining areas of abrasive rupture, bruises and cracks Dark spiral lines appearing as the washings were repeated indicated an increasing chemical tendering effect

The results of tensile strength and fluidity tests for the series laundered in 1940 cannot be compared with those obtained for the series laundered in 1948 The effect of 100 washings as recorded for the gyrator machine with wringer in 1940 was not the same as that for the automatic machine in 1948, nor did it differ in any consistent manner *

The damage to the fibres in these two series as shown by the Congo Red test, however, may be compared, if no strict pairing is made of samples of old and new pieces from any one level of washing The unlaundered controls were similar in appearance, that from the 1940 series showing little of the weakening effect of age which was indicated by the tensile strength and fluidity changes over the eight years storage period A prevalence of tiny, irregular cracks, noted in the samples from the 1940 series, was not found to the same extent in fibres from the series laundered in 1948 These gave to the fibre an uneven outline and a damaged appearance which has been referred to as an "all-over" tendering This difference was much more noticeable at higher washing levels than in the controls, it is an effect which was general for such aged fabrics as have been examined, and may be ascribed to ageing alone It must be remembered that such an observation cannot be made a conclusion from laundered material in which damage was so complex, and where minute comparison with fresh laundered material was not possible

CONCLUSIONS

The Congo Red technique, by revealing rupture of the fibre cuticle, indicated the extent of mechanical weakening and the effect of chemical tendering produced by laundering cotton sheeting The wear was most apparent after 50 washes, when areas showing chemical tendering were coupled with

---

* This difference in washing effect was not merely the result of dissimilar machine action A series duplicating that laundered in the automatic machine and using the same material was subjected to 25 launderings in the same gyrator machine used for the 1940 study following the same method Test results at 10 and 25 washes indicated a lowering of tensile strength but no change in fluidity in this series as well, the effect given by laundering in the automatic machine in 1948, but not in the gyrator machine in 1940 The divergence in washing effect would therefore seem to be caused by variation in material, drying methods, or other factors distinct from the introduction of a different machine

those mechanically damaged. A qualitative relation only was noted between the degree of deterioration of the fibre and any specific number of washes. The unlaundered controls were characteristic of fabric bleached but unused, while samples from the 50 to 100 wash levels were recognizable by the degradation characteristic of many launderings

This test would be valuable in investigation of wear in clothing and household textiles to show the types of damage present, and to identify areas of special injury. It would not indicate any exact degree of damage sustained, but would give information of considerable interest to the general study of wear as it affects the fibres of cotton goods.

SUMMARY

Damage sustained by cotton sheeting laundered up to 100 times was investigated. Tensile strength and fluidity were determined after 0, 10, 25, 50 and 100 launderings. Differential staining using the Congo Red test traced progressive chemical and mechanical tendering of the fibre cuticle

Samples laundered in 1940 in a gyrator machine extracted with wringer showed a higher fluidity and a lower tensile strength at all washing levels when re-tested in 1948 This tendering was ascribed to ageing, as were certain uneven cracks visible in the stained fibres from this series Samples dried outdoors in 1940 still gave higher fluidity and lower tensile strength values in the determinations made in 1948 than those dried indoors No difference was visible between outdoor and indoor dried pieces using the Congo Red test.

A similar series laundered 100 times in an automatic machine in 1948 demonstrated progressive wear effects Tensile strength was lowered after 10, 25, 50 and 100 washes, fluidity values rose only after 50 washes. The Congo Red test indicated a gradual increase in mechanical rupture of the cuticle, with both chemical and mechanical damage prominent after 50 and 100 washings.

Use of the Congo Red test revealed a characteristic appearance in fibres from unusued fabric, and from material laundered many times, but no strict relation could be found between the microscopic aspect and specific fluidity or tensile strength values Further study employing this technique is suggested to extend knowledge or areas of special injury in worn garments.

ACKNOWLEDGEMENT

The writers wish to thank Dr. A C. Goodings, who made available the Conditioning Room and Scott Tester of the Ontario Research Foundation, and Mr C H. Bayley, of the National Research Council, York Knitting Mills, Toronto, Dominion Textile Co Ltd , Montreal, and the U S Dept. of Agriculture, who aided the investigation by supplying many of the materials needed The photomicrographs were prepared at the Department of Botany, University of Toronto

REFERENCES

[1] Anderson and Kerr *J. Ind Engng Chem* , 1938, 30, 48
[2] Berkley. *Text Res J* , 1939, 9, 355
[3] Berkley *Text Res J* , 1948, 18, 71
[4] Clegg *J Text Inst* , 1940, 31, T47
[5] Hock, Ramsay, and Harris *Am Dyestuff Reporter*, 1941, 30, 53, 75.
[6] Kerr *Text Res J* , 1946, *16*, 249
[7] Rollins *Text Res J* , 1945, 15, 65.
[8] Sisson. *Text Res J* , 1933, 3, 242

Received 11/10/48

ILLUSTRATIONS

Low power magnification (×100) was used for some of the photomicrographs in order to show a representative variation in the type and degree of damage met at each level of wear Areas of interest and significance were photographed using a higher magnification (×200)

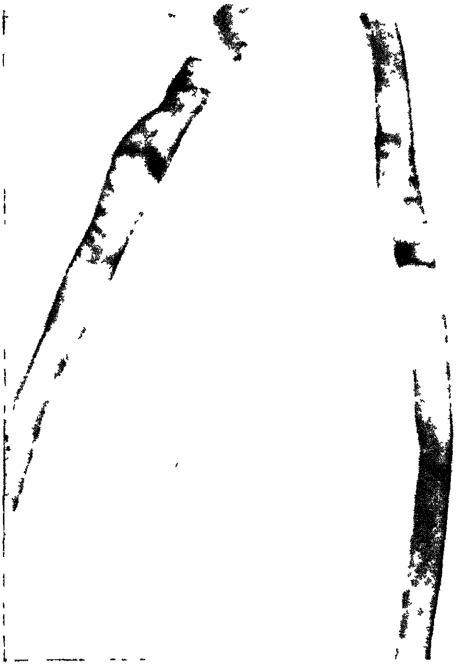

Plate I (1).
Raw Cotton, Stoneville 5 Year Crop 1935
(×200)

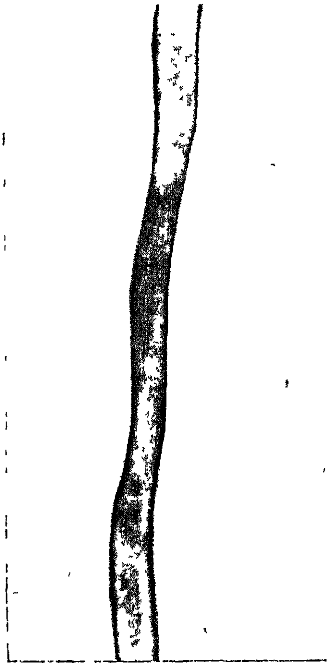

Plate I (2)
U S D A Raw Cotton Stoneville 26
Year Crop 1937 (×200)

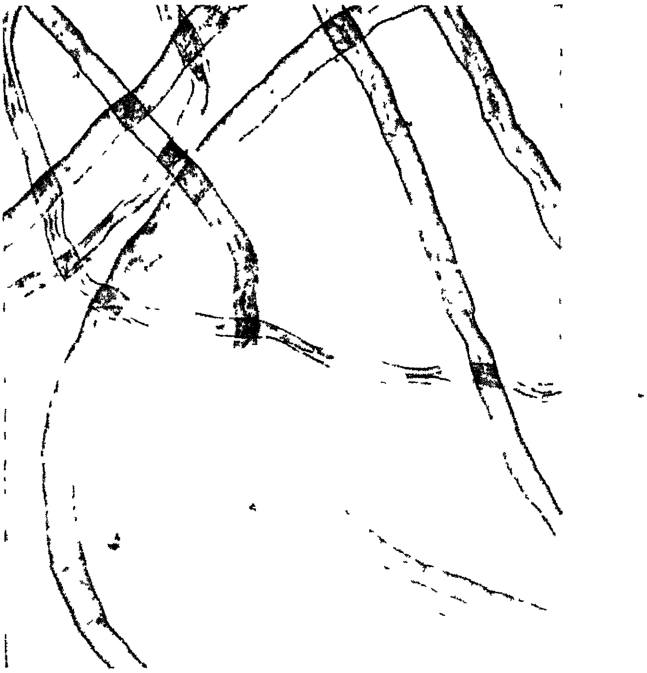

Plate I (3)
Unlaundered Cotton, 1948 Series (×100).

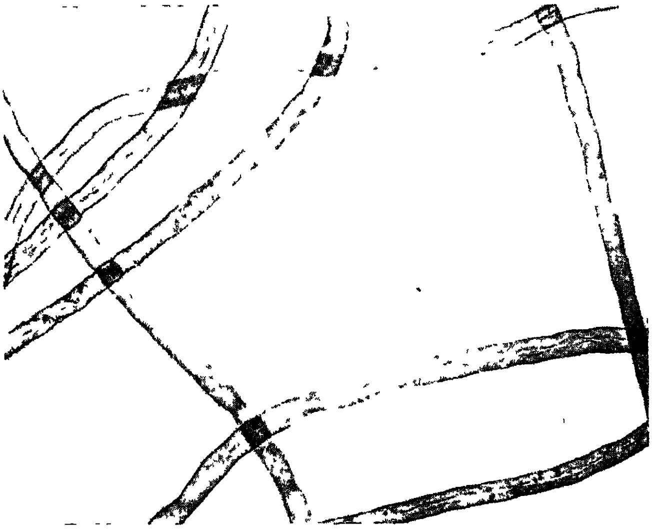

Plate II (4).
Unlaundered Cotton, 1940 Series
(×100)

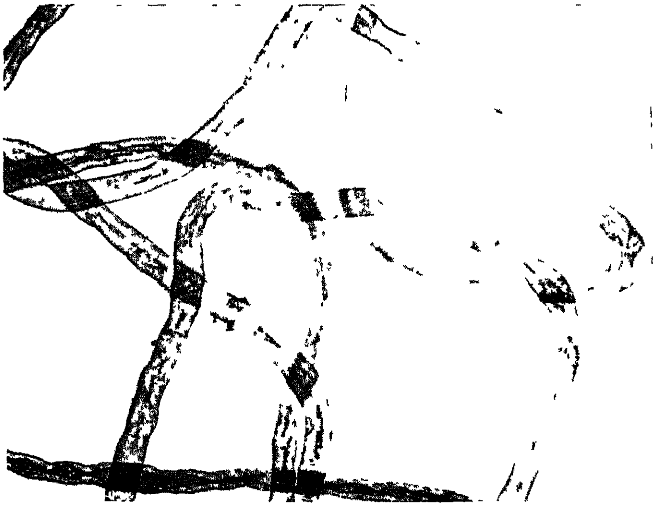

Plate II (5)
Cotton laundered 10 times in 1940
(×100)

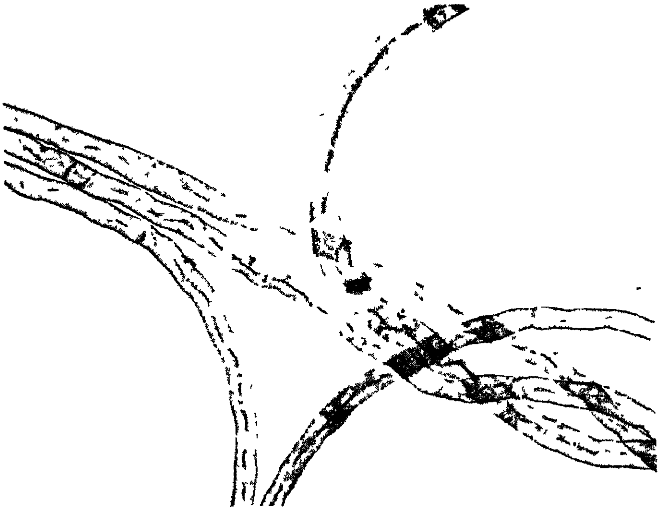

Plate III (6)
Cotton laundered 25 times in 1940 (×100)

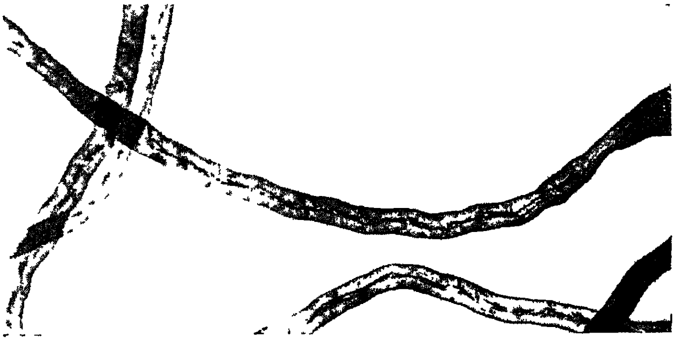

Plate III (7)
Cotton laundered 50 times in 1940 (×100)

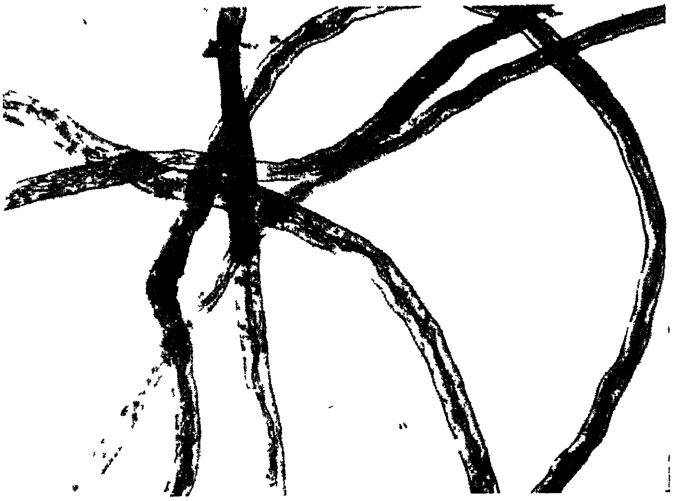

Plate III (8).
Cotton laundered 100 times in 1940 (×100)

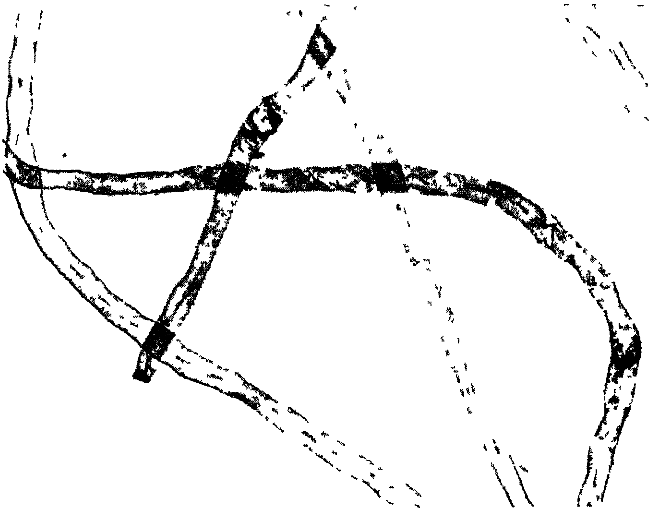

Plate IV (9)
Cotton laundered 10 times in 1948
(×100)

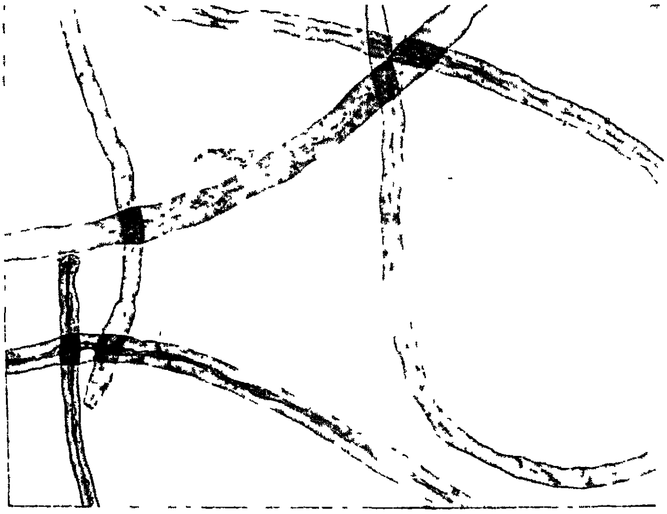

Plate IV (10)
Cotton laundered 25 times in 1948
(×100)

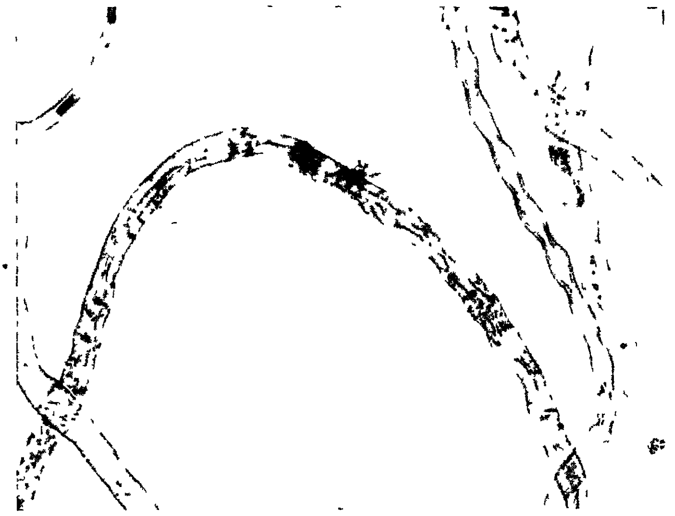

Plate V (11)
Cotton laundered 50 times in 1948
(×100)

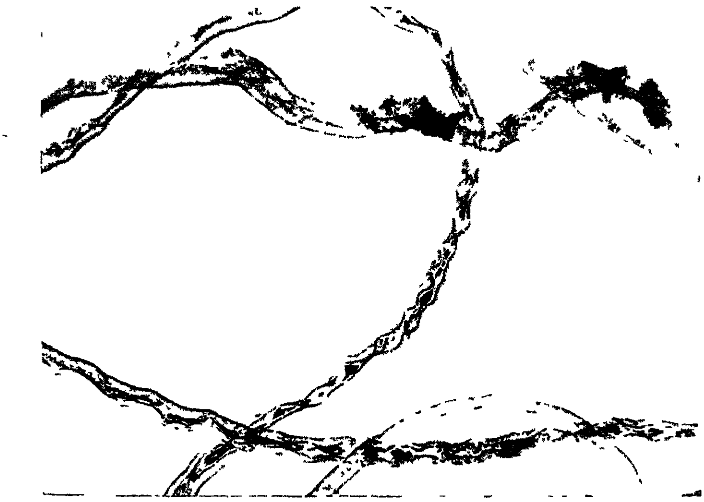

Plate V (12)
Cotton laundered 100 times in 1948
(×100)

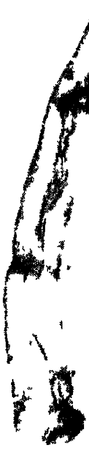

Plate VI (13)
Unlaundered Cotton, 1940 Series
(×200)

Top Plate VI (14)
Cotton laundered 100 times in 1940
(×200)

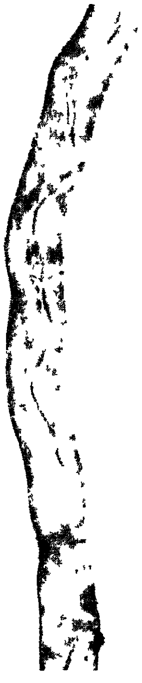

Plate VI (15)
Unlaundered Cotton, 1948 Series).
(×200)

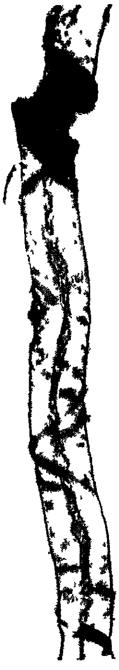

Plate VI (16)
Laundered 100 times in 1948
(×200)

Letters to the Editor

[*The Institute is not responsible for the opinions of correspondents*]

To the Editor, *Journal of the Textile Institute*

INTERNAL WETTING OF FIBRES AS A FACTOR IN DETERGENCY

It is generally accepted that efficient detergent action cannot be obtained unless there is complete wetting-out of the fabric by the detergent solution. The term "complete wetting-out" has generally been interpreted as meaning the penetration of the solution into the spaces between the yarns of the fabric and also into the smaller interstices between the individual fibres of each yarn.

During the course of an investigation of the contours of very small oil drops adhering to textile fibres immersed in detergent solutions we have obtained data which indicate that penetration of the solution into the internal micro-capillary regions of individual fibres may also play an important part in detergent action In this preliminary note some typical photo-micraphs are given which, we believe, illustrate a factor in the mechanism of detergency which has hitherto received little attention

EXPERIMENTAL

The experimental procedure consisted of mounting horizontally a short length (1 cm) of purified fibre between two vertical supports attached to the cover of a small optical glass cell The ends of the fibre were fixed to the support by means of paraffin wax, and the fibre was coated with an oil film by gently stroking it with a fine glass rod which had been dipped in liquid paraffin ("Nujol") The mounting was then placed in the glass cell containing the detergent solution and set in position on the microscope stage. Projection of the fibre to a magnification of approximately 300 diameters for continuous observation and photographic purposes was made by the usual technique Most of the oil film was removed from the fibre during the process of immersion, but a few (10-20) very small and strongly adherent oil drops, having diameters of the same order as that of the fibre, remained.

RESULTS AND DISCUSSION

Although the original object of the investigation was to examine the contours of such oil drops when solutions of different interfacial tensions were used, it soon became apparent that a time factor was involved and this was traced to the formation of air bubbles within the oil drops, produced by the ejection of air from the internal regions of the fibre at those parts of the fibre surface covered by the oil After several hours immersion in the detergent solution, the amount of air displaced from inside the fibre into the oil drops was in many instances sufficient to increase their buoyancy to such an extent that they could be shaken off by the slightest agitation Many hundreds of observations were made using wool, cotton and kapok fibres The effect was found to be quite general, although the rate and extent of inflation varied according to the type of fibre and the number of residual oil drops on the 1 cm length

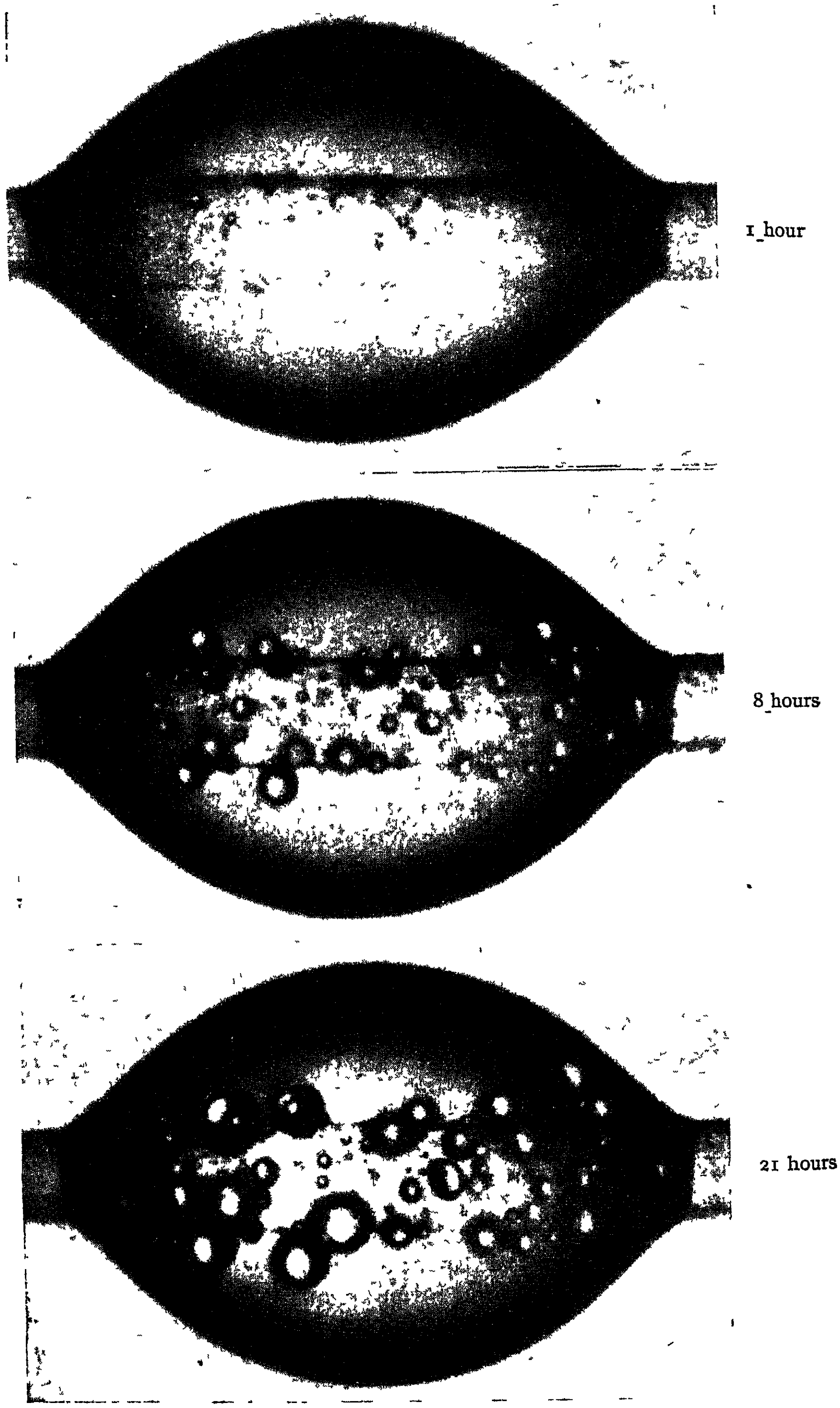

Fig 1
Oil drops on wool fibres in detergent solution (Magnification × 300)

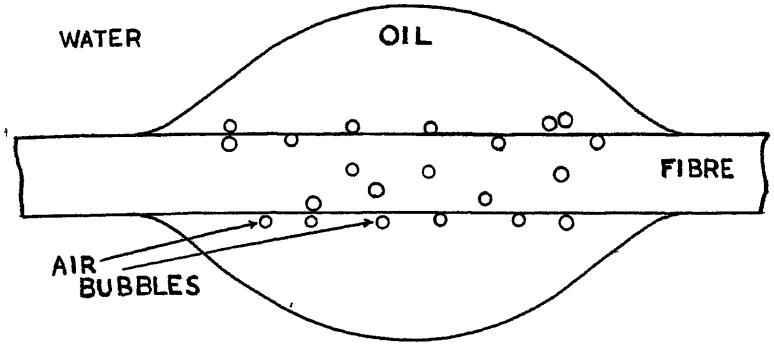

Fig 1A

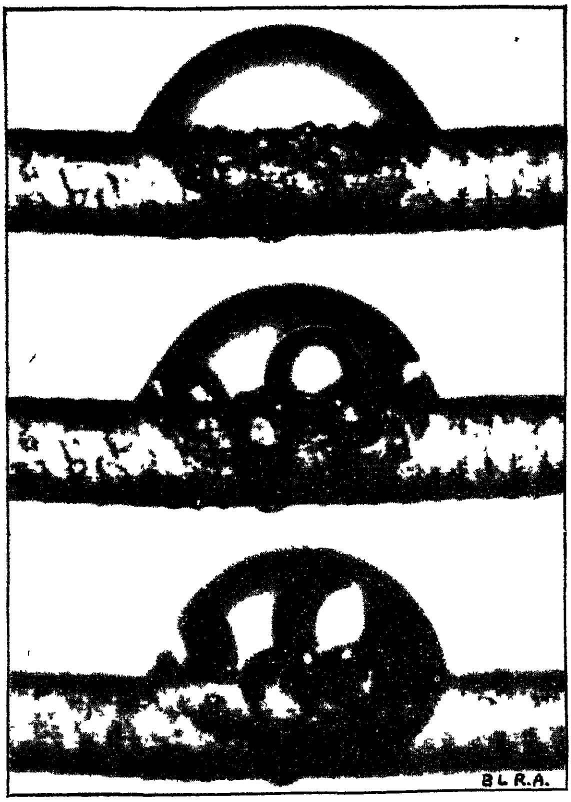

Fig 2
Oil drops on wool fibres in detergent solution (Magnification ×300)

The examples shown in Figs. 1-4 were all obtained using a solution of an alkyl sulphate detergent having an interfacial tension of 10 dynes/cm against the oil, and a *pH* value of 6·5. Fig. 1 is given because it shows clearly the individual development of air bubbles within the oil. The oil drop is here much larger than those we are generally considering, and there is little distortion due to the air. The line drawing, Fig. 1a explains Fig. 1.

Another wool fibre with a very much smaller oil drop attached is shown in Fig. 2. In this instance the amount of air ejected is sufficient to produce considerable distortion of the oil drop. It may be mentioned here that when chlorinated or shrink-proofed wool was used, the same evolution of air bubbles was observed, but the rate was very much greater. Fig. 3 is typical of many cotton fibres studied and was obtained after 12 hours immersion. No further change occurred on prolonged soaking. It is of interest to note that although both oil drops were originally the same size, approximately,

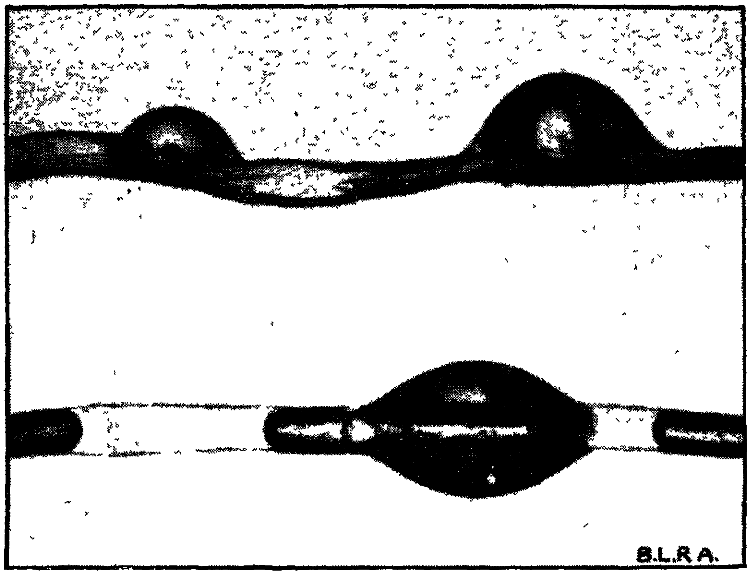

Fig. 3 (*above*)
Oil drops on cotton fibre in detergent solution after 12 hours

Fig. 4 (*below*)
Oil drops on kapok fibre in detergent solution after 1 hour
(Magnification ×300)

only a very small air bubble was formed within the left-hand drop which is seated exactly on a "twist" in the cotton fibre in contrast to the considerable inflation of the right-hand drop which covers a flat portion of the fibre. This selective behaviour was noted on many occasions.

If a very thin walled fibre such as kapok is used (Fig. 4), the penetration of the solution into the internal channel and the displacement of air into the oil drop can be directly observed. In this example equilibrium is reached within one hour, but the experiments with kapok are difficult to perform owing to the fragile nature of the fibre.

It is tentatively suggested that the mechanism of the effect described above consists of the penetration of water into the fibre at the "clean" surface on either side of the oil drop and that under the conditions stated, the oil is incapable of penetrating the fibre capillaries. Air locks are thus set up which slowly release their pressure through the only means of escape, namely, the oil-covered capillary orifices of the fibre.

In conclusion it may be mentioned that a few experiments have been carried out using water only, the general result being that for wool fibres the rate of air bubble formation is reduced considerably, but that for cotton or kapok there is little change.

It is clearly necessary to examine the effect in more detail, particularly with regard to *pH* and associated swelling of the fibres. The data so far obtained were thought worthy of record, since it is a practical fact that certain types of resistant soil which are not removed from fabrics by normal washing processes can be removed by a prolonged soaking process. By a more refined technique it may also be possible to estimate the internal free space of certain textile fibres.

Further work is to be undertaken on this interesting aspect of detergency.

ACKNOWLEDGEMENTS

The author wishes to express his thanks to the Director of Research for his advice and interest and to the Council of the British Launderers' Research Association for permission to publish this work.

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To the Editor, *Journal of the Textile Institute*

DESOILING PROPERTIES OF CARBOXYMETHYL CELLULOSE

The ability of sodium carboxymethyl cellulose (CMC) to reduce deposition of soil from detergent solutions has been fairly conclusively established[1,2,4,5]. However, Nieuwenhuis (private communication) expressed the view that CMC might additionally possess definite desoiling properties, and certain results obtained in these laboratories were similarly suggestive of such an effect. As, in these results, it was difficult to differentiate unequivocally between the known suspending power of CMC and its possible desoiling power, a special investigation was carried out.

Using the chopped fibre technique[6] 1·5 gm. samples of cotton containing 1 per cent. colloidal graphite and 6 per cent. Nujol were washed for 20 minutes at 60° C. in 300 ml. of a solution (A) of 0·1 per cent. Lissapol N and 0·1 per cent. sodium metasilicate, and in a similar solution (B) containing in addition 0·05 per cent. Tylose HBR (German CMC). After the usual rinses, mounts were prepared as described[6]. Further 1·5 gm. samples of the cotton were washed in solution (A) as above and then given two 3-minute rinses at 60° C. in 300 ml. water. These washed and rinsed fibres were then immediately re-washed in various solutions as follows:—

(C) distilled water
(D) 0·1 per cent sodium metasilicate
(E) 0 05 per cent. Tylose HBR
(F) 0 1 per cent sodium metasilicate+0 05 per cent Tylose HBR
(G) 0 1 per cent Lissapol N+0 05 per cent Tylose HBR
(H) fresh solution (A)
(I) fresh solution (B)

These re-washes were followed by the standard rinsing and mounting procedure. Two replications were made.

The results, expressed as percentage reflectance in terms of unsoiled chopped fibres[5,6] are given in Table I A simple variance analysis showed a highly significant difference "between columns" ($F=66\ 6$ for d f $n_1=8$, $n_2=9$ $P<0\ 001$) The standard error of the means and the minimum difference required for significance at the $P=0\ 05$ level were obtained by using the "within columns" mean square as an estimate of error

Table I

	A	B	C	D	E	F	G	H	I
	57·0	72 8	56 2	54 3	56 8	54 0	77 1	68 7	78·5
	59 1	75 3	52 8	57 6	57·9	56 5	76 7	72 6	78 4
Mean .	58 0	74·0	54·5	55 9	57 3	55 2	76 9	70 6	78 4

S E. of each mean . 1 2
Minimum difference for significance (P=0 05) 4 0

The mean value for A represents the limiting result for a single wash in this solution and it is seen that re-washing in solutions C-F had no significant effect The improved result for B as compared with A was interpreted as being predominantly a typical CMC effect of reducing redeposition, for the following reason From previous work in these laboratories the relationship between the soil content of the fibres and their reflectance was known with fair accuracy It was thus possible to calculate that the amount of removed soil present in solution A during the single wash was of the order 14 mg (per 300 ml). Separate experiments using unsoiled fibres showed that redeposition of about 0 5 mg soil could occur from such a suspension, and this, within the limits of error, accounted for the 16 per cent difference in reflectance between the mean values for A and B

By re-washing in solutions G, H, or I more soil was removed, and it is noted that solutions G and I, each containing CMC gave results significantly better than H These results, as they stand, do not establish unambiguously the soil removal powers of CMC, for a non-redeposition effect (as for A *v* B) is still a possible alternative explanation. But there was a very important difference between the A *v* B and the G and I *v* H conditions, inasmuch as the concentrations of soil in suspension and available for redeposition were greatly dissimilar Re-washing *in solutions G or I removed not more* than a further 0 6 mg soil, which, of course, passed into suspension in a fresh liquor. Separate experiments showed that no measurable deposition on to unsoiled fibres took place from a suspension of 0 6 mg soil in such a liquor, *i e* 300 ml of solution A An explanation of the differences between G and I compared with H in terms of redeposition would have required the deposition of about 0 25 mg of soil, and the resulting 8 per cent reduction in reflectance should have been detectable Redeposition from such weak suspensions would in any event be unlikely from considerations of mass action, for whereas in solution A about 3·5 per cent of the total soil was redeposited, the G, H, and I differences on the redeposition explanation would have required the deposition of 40 per cent. of the soil contained in a suspension 20 times more dilute.

It may be pointed out that the improved result for G, as compared with H, cannot be explained as a sodium ion or "builder" effect on the detergent, for although Tylose HBR, in addition to being a sodium compound, contains sodium chloride and carbonate as impurities, the Na′ ion concentration due to this substance in G did not exceed 0·0035 N, whereas in H the corresponding concentration produced by the metasilicate was 0·0094 N, and yet H was significantly inferior to G.

It seems therefore that CMC enhances the desoiling power of the particular non-ionic detergent used, although it does not itself possess soil removal properties and does not appear to function as a simple "builder". The effect is admittedly small, but on the other hand the removal of the last traces of soil is of considerable importance in practical applications of detergency. The mechanism is at present unknown, and further investigation, particularly with other types of synthetic detergents, is desirable It is possible that some kind of exchange reaction, as in McBain's equation[7] may be involved. Thus, initially, CMC may be adsorbed to form a fabric-soil-CMC complex, which is subsequently split at the first linkage by the detergent, yielding fabric-detergent and soil-CMC-detergent complexes.

The author wishes to thank the Director of Research for his valuable advice and criticism and the Council of the British Launderers' Research Association for permission to publish this note

REFERENCES

[1] Nieuwenhuis, K. J., *Chem. Weekblad*, 43, 510 (1947).

[2] Vaughn, T. H and Smith, C. E *J Amer. Oil. Chem. Soc.*, 25, 44 (1948).

[3] Armstrong, L. J. *et al.* *Amer. Dyestuff Reporter*, 37, 596 (1948).

[4] Bayley, C H., Weatherburn, A. S and Rose, G. R. F. *Laundry and Dry Cleaning Journal of Canada*. 28, No. 12, p 16 (1948)

[5] Feuell, A. J and Wagg, R. E. *Research*, 2, 334 (1949)

[6] Powney, J and Feuell, A. J. *Research*, 2, 331 (1949)

[7] McBain, J W "Advances in Colloid Science" p 115 *Interscience* New York (1942).

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To the Editor, *Journal of the Textile Institute.*

A Suggested Method of Testing Woven Fabrics for Measurement of Resistance to Slippage of Warp Threads over the Weft, or Weft over the Warp

Owing to an enquiry which I have recently received regarding seam slippage in a garment made from a rayon warp satin fabric, I have been interested in the proposed method of test communicated by a letter in the April issue of the *Journal*

Since slippage is a property of the fabric itself it is evidently correct that this property should be tested on the fabric itself, by measurement of the force required to cause the slippage of one set of threads over the other set, without introducing any question of seaming. In stating this principle the author of the letter has realised the essentials of the test and has freed it from the unnecessary complications of seaming.

In assessing the liability of a fabric to slip, a good estimation may be made manually, by using the finger and thumb in dragging one set of threads over the other. A test method which reproduces this effect under mechanically controlled conditions, and gives a numerical result which measures the force of drag, is therefore the best criterion.

The method suggested in the letter appears to fulfil all requirements, being sound in principle and simple in practice, and in my opinion it might be developed into a standard test for fabric slippage.

J. LOMAX.

City of Nottingham Textile Testing Bureau.

THE JOURNAL OF THE

TEXTILE INSTITUTE

TRANSACTIONS

32—THE PRODUCTION AND CHARACTERISTICS OF THE WORLD'S COTTON CROPS

Part 3. SUDAN

By E. LORD

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INTRODUCTION

For many years Egyptian cotton has held a high reputation among spinners, especially by virtue of its excellent quality which enables it to be spun into strong, fine regular yarns. Egypt is, of course, the largest producer of this style of cotton and the growth and characteristics of the Egyptian crop have been described in the second of this series of papers. Although Egypt is by far the largest exporter of Egyptian-type cotton, in the past fifteen years the Anglo-Egyptian Sudan has also firmly established itself in this market. It is therefore appropriate to devote the third paper in this series* to an account of the cotton crops of the Sudan.

Cotton appears to have been grown in some parts of the Sudan for local consumption for at least 2,000 years, but only in comparatively recent times has the crop been produced for commerce. Between 1911 and 1920 the annual exports of Sudan cotton were usually between 15,000 and 20,000 bales † In 1923 the crop had risen to about 28,000 bales and, following the extension of the irrigation system, to 122,000 in 1926.

Immediately previous to the outbreak of war, the total Egyptian crop averaged about 2,000,000 bales and the production of Egyptian cotton in the Sudan had risen to about 250,000 bales. These figures do not wholly illustrate the relative importance of the two crops. In the 1938/39 season Egypt produced some 190,000 bales of long-staple Egyptian cotton (Malaki, Sakel, Sakha 4 and Maarad), 540,000 bales of medium-staple Egyptian (mainly Giza 7) and 1,300,000 bales of the "bread-and-butter" Ashmouni/

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* Part I, "The West Indies" appeared in *Shirley Inst Mem*, 1945, 19, 315 and *J Text Inst*, 1946, 37, T151, and Part 2, "Egypt," in *Shirley Inst Mem.*, 1946 20, 21 and *J Text Inst*, 1947, 38, T167.

† As in the previous papers in this series, production figures refer to the 'statistical bale of 400 lb. and not to the size of the normal 'running' bale. Gezira and Gash bales average about 430 lb gross, Tokar ginned at Suakin about 600 lb and at Port Sudan 430 lb, Zeidab usually 440-450 lb., and rain-grown American Seed NM 220-285 lb., MER 220 lb.

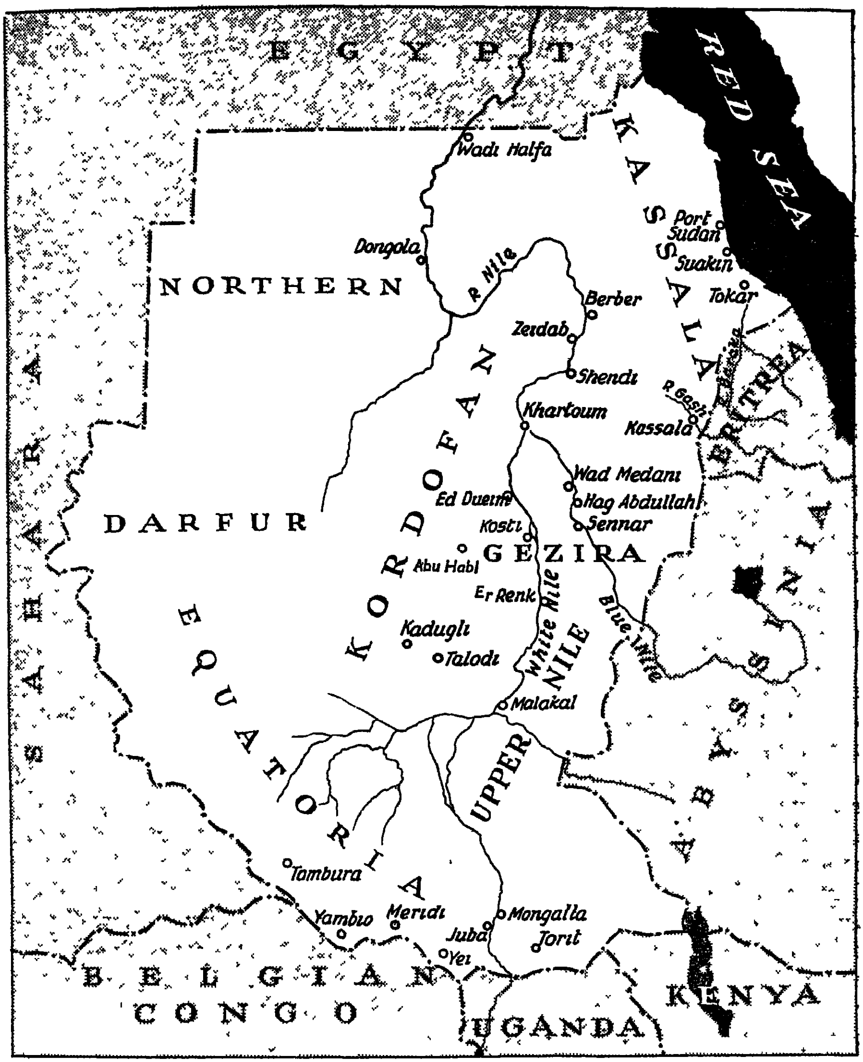
Zagora crop. In the same season the production of Egyptian cotton in the Sudan, all of Sakel type, amounted to about 265,000 bales. Thus more long-staple Egyptian cotton was grown in the Sudan than in Egypt itself.

During the war, however, the position radically altered. The size of the Egyptian crop declined because of restrictions upon, and greatly reduced demands for, the Ashmouni/Zagora cotton. This change was accompanied by an expansion in the production of high-quality long-staple cotton. The new Karnak variety was introduced and its cultivation rapidly spread from 1939/40 onwards. By 1943/44 the production of fine long-staple Egyptian cotton had risen to about 500,000 bales, compared with about 300,000 bales of Sudan Sakel The demands for Egyptian cotton have now changed somewhat: the need for long-staple cotton is smaller and there is an increased demand for the medium- and short-staple types When conditions return more closely to normal it remains to be seen whether the demand for Karnak declines, whether Egypt will again concentrate upon a large crop of medium-staple cotton and the Sudan will again take first place as the largest supplier of Egyptian-type long-staple cotton.

The Sudan also produces American-type cotton, although on a smaller scale than Egyptian Immediately prior to the war, the crop amounted to about 10,000 bales of Irrigated Sudan American and about 30,000 bales of Rain-grown Sudan American. During the later stages of the war the production of American cotton was greatly curtailed and is still low. The irrigated crop is now only about one-third of the pre-war quantity. The rain-grown crop of Kordofan Province remained low for the first three post-war seasons In the 1948/49 season, however, there was a marked increase in production and the crop was treble that of the previous season There are good prospects that this area will soon pass its previous peak

The object of this series of papers is to provide a general but comprehensive account of cotton and its growth in the different areas of the world. Consequently, this paper gives not only a full description of the commercial Sudan Sakel and Sudan American crops, but also provides many details of other strains as yet in the experimental stages of development in the Sudan. Information regarding the former cottons is mainly of use to the spinner: the latter cottons are more particularly of interest to breeders and growers in the Sudan and also in countries where changes in seed supply are being considered. The experimental strains are also the concern of the spinner because he is ultimately affected by the course of current development It is from this material that ultimately will emerge the nucleus stocks for the bulk propagation of future commercial crops. Details of agricultural conditions, incidence of disease and insect pests, *etc* , are given in order to develop a background of knowledge for the appreciation of present difficulties and problems, and to understand why workers in the Sudan are directing research along particular channels

To maintain the general descriptive nature of this series of papers, it was decided that it would be inadvisable to provide specific references to the source of each fact and feature mentioned. It would be extremely difficult to segregate satisfactorily much of the detailed information obtained from published papers and reports, from that gained through many valuable discussions with various persons of long experience in the Sudan, and from personal experience gained at the Shirley Institute It is hoped that the general references given in the text will be adequate to indicate where, and by whom, the major portions of the work have been conducted Nevertheless, it is desired to draw especial attention to the acknowledgements at the end of this paper, to the various organisations and individuals directly responsible for much of the current research and crop development in the Sudan, and but for whose help this paper would lose much of its value.



I. ECONOMIC GEOGRAPHY

The total area of the Sudan is about one million square miles, more than half the area of India. It extends from the southern limits of Egypt to the borders of the Belgian Congo and Uganda, and is bounded by French Equatorial Africa in the west and in the east by the Red Sea, Eritrea and Abyssinia. At one time the population of the Sudan is estimated to have been about 10 millions, but wars and devastations at the time of the Mahdi and the Khalifa reduced this figure to 2 millions With the settled administration in the present century the population has rapidly increased and now exceeds 6 millions.

Sakel cotton is grown in three main areas of which the most important is the Gezira, a triangular-shaped plain bounded on the west by the White Nile, and on the east by the Blue Nile. (See map.) The apex of the triangle is at Khartoum, the junction of the two Niles, and the railway line from Sennar to Kosti forms the southern base. Here the cotton crop is grown under perennial irrigation, mainly from the barrage across the Blue Nile at Sennar, but in some places from pumps drawing water from the White Nile. The Gash and Tokar regions, respectively east and north-east of the Gezira, are watered by flood irrigation from annual risings of seasonal rivers.

The main crop of American cotton is grown under rainfall conditions in the Nuba Mountains in Kordofan Province. Near the south-eastern limits of Kordofan is a recently developed small flood irrigation project of Abu Habl, which has proved valuable for raising stocks of multiplication seed, because it is isolated from the other cotton areas of this region. Another, but much smaller, rain-grown American crop comes from Equatoria, in the extreme south of the country, whilst rain-grown cotton was raised until a few years ago in the Upper Nile Province. There are also a number of pump schemes in the Northern Province on which crops are grown under irrigated conditions, but on only one of these is cotton now produced in quantity

(*a*) SUDAN SAKEL AREAS.

(i) The Gezira

The Gezira plain covers about 5 million feddans* and is extremely flat, mainly between 1,240 and 1,300 feet above sea level. A low ridge of ground runs roughly north and south, somewhat to the eastern side of the centre. This ridge determines the limits to which it is possible to extend gravity-flow irrigation. The soil is a heavy brownish type of clay, very impervious to water, rather salty and alkaline, and having a low content of nitrogen and organic matter

The short summer rains occur mainly in July and August. The rainfall is heaviest in the south, amounting to about 17 inches at Sennar, and becomes smaller in a northerly direction until at Khartoum it averages only 6 inches per annum. Although only small the rains permit the growth of grasses and dura (millet). Then follows a long period without growth and the land is virtually featureless. The soil dries up and this results in marked shrinking and widespread deep cracking. These cracks may go down as much as five or six feet in a single season. Finer cracks branch off from the major fissures and permeate the whole mass of the soil. The result of alternate shrinkage and expansion is that the soil breaks up into dust and small particles. Wind and casual rain result in much of the finer parts of the broken-up soil being swept down the cracks with the result that the top two feet of earth undergoes light natural tillage. Only a minimum of cultivation is usually necessary to obtain a good tilth on this heavy soil.

Proposals for growing cotton in the Sudan by perennial irrigation date back to 1904 when an American, Leigh Hunt, visited the country and obtained a concession at Zeidab, some 180 miles north of Khartoum. The "Sudan Experimental Plantations Syndicate" was formed in London to develop this concession. Negroes were introduced from America to work on the scheme. No success attended these initial trials and the negroes had to be taken back to America. In 1906 the syndicate was reorganised as the "Sudan Plantations Syndicate". The total size of the concession amounted to about 10,000 feddans, and the first crop produced under the direction of the new Syndicate was raised on 100 feddans in 1906. This crop was grown under irrigation, by pumping water up from the level of the Nile, and gave a satisfactory yield.

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*1 feddan = 1·04 acres.

Meanwhile, economic development of the Sudan was being pushed forward. The railway from the north was extended southwards from Khartoum and had reached Wad Medani on the Blue Nile by 1910 Serious consideration was then given to the feasability of growing large crops of cotton in the Gezira, especially according to established Egyptian methods.

In 1910 agreement was reached between the Sudan Plantations Syndicate and the Sudan Government, whereby a further concession was granted, this time at Tayiba, on the Blue Nile a few miles north of Wad Medani. Here a pump station was built and 3,000 feddans brought under irrigation. In 1913 a second pump scheme was started and an area of about 6,000 feddans developed at Barakat, just south of Wad Medani.

By 1914, experience at Tayiba had shown that cotton could be successfully grown under irrigation in this area, and the Barakat scheme was extended. The Government began to formulate plans to erect a dam near Sennar, to draw off water from the Blue Nile and use it to irrigate an area covering 300,000 feddans, of which each year one-third would be under cotton.

The Egyptian cotton crop is planted from about the middle of February to the end of April. Results obtained at the experimental station near Khartoum showed that in this region the most favourable months for cotton sowing are July and August. Since Egypt's water requirements are more than fully met by the Nile flow from July to December, it was clearly practicable for the Sudan to make use of surplus water and grow cotton as a winter crop without causing any serious repercussions

The 1914-1918 war postponed the building of the Sennar dam, but the scheme was re-considered immediately afterwards. As a start, large pumping stations were established at various places along the Blue Nile, at Hag Abdullah in 1921 and at Wad-el-Nau in 1923. The inauguration of these pump stations enabled a start to be made in the preparation of land and in the training of the native population in the methods of agriculture. Valuable general experience was gained before the whole scheme came into operation.

The Sennar Dam was finished in 1925, at Makwar, a few miles south of Sennar, where the rocky bed of the Nile provides a firm foundation. The Sennar Dam acts partly as a reservoir, to store water for use in the period of low Nile, and partly as a barrage to raise the level of the river to a height such that a main canal will take off water to irrigate the area by gravity flow. The first crop of cotton was sown in this year on 80,000 feddans out of the total of 300,000 available for irrigation.

In subsequent years more land was steadily brought under irrigation and now the whole scheme covers about 900,000 feddans, more than 200,000 of which are under cotton each year. This area runs in a strip along the western side of the Blue Nile for roughly 120 miles, measuring about 40 miles wide in the centre and narrowing at each end to about 6 miles.

So far the scheme has been operated under a tripartite profit-sharing partnership. The Government was responsible for the building of the dam, the construction of the major canals and for providing the water. The Sudan Plantations Syndicate constructed the minor canal system, leading off from the main canal and its branches, and is responsible for carrying out the first ploughings, supervision of the cultivation of the crop, purchasing the seed cotton from the cultivator, ginning, storing and marketing. The native growers are allotted tenancies of 40 feddans, of which 10 are placed under cotton each year. They are responsible for ridging of the land after ploughing, and for sowing, cultivation, picking, *etc.*

After ginning and marketing costs have been met, the proceeds of the crop are divided between the three parties. The Government take 40 per cent. of the money to cover interest on the capital outlay of the undertaking and to add to the revenues of the Sudan, the cultivator also receives 40 per cent, and the Syndicate 20 per cent. When the Kassala Cotton Company (see later) gave up its concession in the Gash area it received in return a concession on one of the extensions of the Gezira Scheme, on the extreme western side of the centre. For convenience in supplying irrigation water the land under cultivation is divided into 39 blocks, varying in size according to the nature of the land. Most of the blocks cover from about 20,000 to 30,000 feddans each. The Sudan Plantations Syndicate controls 33 blocks and the Kassala Cotton Company 6 blocks

The northern blocks grow the Domains Sakel strain of cotton, and the southern blocks grow the X 1730A strain, known commercially as the "S" and "L" types, respectively. In the centre some blocks grow Domains Sakel and others grow X 1730A.

The joint concession is due to terminate in 1950 and the present intention of the Government is that it shall take over the functions of these two companies and run the whole scheme, possibly under the direction of some form of Control Board.

There is a second dam in the Gezira area, at Jebel Aulia on the White Nile, some 30 miles from Khartoum. The purpose of this dam is not to irrigate areas in the Sudan, but to store and control water for Egypt The building of this dam caused many holdings upstream to be inundated and the Sudan Government inaugurated the White Nile Alternative Livelihood Schemes to cater for the displaced cultivators. The most important of these recently established areas is that of Abdel Magid, in the centre of the northern part of the Gezira and connected to the Gezira irrigation system Fatisa, Hashaba, Um Gerr and Wad Nimr are pump stations on the White Nile forming part of the Alternative Livelihood Scheme Normally Abdel Magid grows about 10,000 feddans of cotton, and about 6,000 feddans are raised in the other areas.

There are other, and older, White Nile pump stations which irrigate about 12,000 feddans of cotton each year. Most of these schemes are privately owned and the largest of them belongs to the Mahdi. This estate lies on Aba Island, north of Kosti where the White Nile branches for about 25 miles down stream. Ed Dueim is another but much smaller station situated still further north

In order to grow cotton under perennial irrigation it is necessary to carry out much more preparation of the land than is the case with annual flood irrigation, as in the Tokar and Gash areas described below. An extensive system of minor canals has to be laid out and the ground ploughed and furrowed. Cultivation is carried out by diesel engines drawing ploughs by cable tackle, although some ploughing is also done by bull-drawn ploughs. Payments are made to the native tenants for any labour supplied in ploughing, but not for the ridging of the land Sowing varies a little in different years but generally begins about August 10th in the northern part of the Gezira and continues until the end of the month. In the centre and south sowing is about five days later and may extend into early September. The crop usually receives three weedings, carried out with ordinary native hoes or, in some cases, by bull-drawn hoes. About fifteen waterings are made in the course of the season, the exact number varying from 12 to 18 according to the prevailing conditions. At each watering the fields are virtually flooded, only the tops of the ridges being above the surface. Broadly speaking, during the cycle of watering operations, the cotton plant may be said to spend one-third of its time in an almost drowned condition, one-third in good growing conditions and the remaining third in very parched soil.

When the Gezira Scheme was first started the land was cultivated on a three-year rotation, a cotton crop, followed by a food or fodder crop and then a fallow year. As a result of co-operative experiments conducted by the Gezira Research Farm of the Department of Agriculture and by the Syndicate it was found that better results could be obtained by an eight-year rotation which includes two cotton, one fodder, and one food crops with the ground under fallow for the remainder of the time. The principal food crop is dura (sorghum millet) which forms the staple diet of the population, whilst lubia is a widely-grown fodder for the feeding of animal stocks.

Land under fallow is allowed to grow annual weeds for the grazing of animals, mainly sheep and goats. During the heat of the summer the weeds on fallow land shrivel up and are easily buried by ploughing. In this respect the Gezira fallow differs from the cleaning fallow practice of many countries. Agricultural experiments at present being carried out in the Gezira suggest that beneficial results to cotton may result from fallow-weeding.

The first pickings are usually in full progress by mid-January. The crop does not mature in a quick rush as in Egypt, where most of the cotton is obtained in two main pickings and possibly a third smaller one In the Gezira up to eight or even ten pickings may be made, several days apart and extending up to mid-April Compulsory uprooting of the crop starts on May 1st to provide a close season for purposes of pest control

(ii) The Gash (Kassala)

The second most important cotton-growing region in the Sudan is that near Kassala, in the province of the same name. Here cotton is produced in the delta of the Gash River, which rises in the foothills of Abyssinia. The river flows through Eritrea and drains a long tract of mountainous country having a heavy but spasmodic rainfall Consequently the flow of the river is very variable Normally the Gash rises in flood about the end of June or early July and runs for about 100 days During this period there are usually numerous spates and the flood waters are effective for about 55 to 60 days. The river spreads out over the delta that it has laid down over a tract extending more than fifty miles north of Kassala, and is eventually lost in the desert sands.

Most of the land capable of being cultivated lies to the west of the main river, but in the south a smaller portion is situated on the east bank The flood waters of the Gash are now largely controlled by a system of main canals which follow the contours of the land and generally run west and east. Smaller canals or *misgas*, running from south to north, branch off the main canals and carry the flood waters over the whole area The delta is divided into 224 hods, each of 4,000 feddans, and each hod is divided into 400 gittas of 10 feddans for the purpose of watering

The rainfall usually varies from about 10 to 16 inches per annum, beginning in July and ceasing in October Since the rains coincide with the floods, the precipitation ceases at an early stage of plant development and mainly adds to the amount of sub-soil moisture, upon which the cotton plant is dependent in this region.

In the delta there are two main types of soil. That known as bardob is a heavy cotton soil, an alluvium of rich black clay. The second type is known as libad and is a light alluvial silt brought down by the flood. The fine libad soil never cracks as does the heavier bardob.

The Gash crop does not receive, nor need, a large amount of cultivation. The area to be sown is first cleared of heavy growth and the inter-misga banks are raised for controlling the flood waters. The whole of the area is not flooded simultaneously, nor is all the land under water for the same length of time. About half of the land intended for cotton is watered for up to 30 days, the lighter libad soils for 7 to 15 days and the heavier bardob for 15 to 30 days. For the next 25 to 30 days the second part of the land then receives water.

The magnitude of the flood varies from year to year and consequently it is not possible to maintain a constant area under cultivation. Moreover, variations in level of the land make it impossible for all areas to be evenly watered. Only well-watered areas can be relied upon to give good yields: the marginal areas are usually placed under dura, a grain crop which demands less water than cotton to give an economic yield Of the total area of 896,000 feddans, much is unsuitable and never cultivated, other parts are resting or under dura, and in recent years the effective area under cotton has averaged about 30,000 feddans

About three days after watering ceases, the highly absorbent soil is usually dry enough for sowing. Sowing, which takes place from mid-August to early September, is done on the flat and a stick is used to lift the surface soil. The rows are about 3 feet wide and the plants are about 3 feet apart along the rows. This spacing is wider than that in the Gezira because cotton grown in the Gash usually makes stronger growth and is of more open habit.

As in the Gezira, two main varieties of cotton are grown, the Domains Sakel and X 1730A strains of Sudan Sakel. In recent years these two cottons have been grown on about equal areas. Especially due north and south of the central tract, X 1730A is often sown on land given the first watering and Domains Sakel on land given the second watering. It has been stated that the later planting of the Domains Sakel reduces risk of infection by leaf curl. Over most of the remainder of the area the land, when under cotton, is frequently planted alternately with Domains Sakel and X 1730A This practice arose because it was thought that the spacing out of crops of Domains Sakel would further reduce the risk of this susceptible variety being infected by leaf curl. South of Kassala, the small area on the east side of the Gash river generally grows only the X 1730A strain

Cotton in the Gash suffers from the same pests and diseases as that in the Gezira. Thrips, leaf curl and asal (a stickiness of leaf caused by aphis) may be severe, and in some seasons pink bollworm results in heavy crop loss. Locusts are always a menace, but are generally kept under control by exceptionally keen and widespread preventive measures. The Gash region is relatively free from blackarm disease, and for many years has been used as a filter propagation area for bulking up seed for the planting of the main Gezira crop. This aspect is described in detail in the later section on Seed Maintenance and Multiplication.

Much of the development of the Gash delta was originally undertaken by the Kassala Cotton Company which received a concession from the Sudan Government and ran the scheme with the native tenants on a profit-sharing basis. Later, the Kassala Cotton Company, which is now closely allied to the Sudan Plantations Syndicate, gave up the concession in the Gash, and in return received a new concession in an extension of the Gezira scheme The Gash scheme is now administered by the Gash Board, the directors of which include the Director of Agriculture, the Governor of Kassala Province and other government officials.

The land is apportioned out among the tenants each year according to the magnitude and spread of the annual flood. Officers of the Department of Agriculture organise the flood irrigation, control the distribution of planting seed and ensure that the cotton is effectively cultivated Picking may begin in December and possibly continue as late as early May. The seed cotton is brought to rail centres for weighing, where the sacks are stacked in lots, according to variety, and advances are paid to the tenants. The Government pays a flat rate for all grades and varieties. This is considered preferable to the making of differential payments because the land is not uniform and some gittas would give poor yields, or low proportions of high grade, despite the most careful cultivation. Later the seed cotton is sent by rail to Port Sudan where it is first graded and then ginned. After the crop has been sold, further payments are made by the Government according to the profit realised on the crop.

(iii) Tokar

Tokar is the third main Sakel producing area in the Sudan and is situated some 100 miles south-east of Port Sudan. In this region the River Baraka has laid down a delta over an area of about 400,000 feddans The river rises annually in flood and rushes down from the mountainous region of Eritrea. When the flatter plain of the Sudan is reached, the flow slackens and large amounts of silt are deposited. The southern end of the delta is largely composed of sandy soil, the heavier component of the silt. Elsewhere the soil consists of the lighter and finer silt, which remains in suspension longer, deposited upon underlying gravel or sand. Near to the coast the land may be so heavily impregnated with salt that cultivation is impracticable, although even this land may improve and grow good crops if it receives the leaching action of several successive floods and the accompanying deposition of new silt Good land is found in patches around the fringe of the delta where layers of silt frequently alternate with layers of sand, or where the silt is covered by the drifting sand In such places cultivation is only possible on occasions of high floods. The area under cotton usually amounts to about 40,000 acres.

The flood waters normally arrive in mid-July and continue until mid-September. The volume of water is not constant and the river may dry up between flushes. The rains (averaging six inches per annum) fall later in the year, but nevertheless it is mainly upon the sub-soil moisture from the floods that the cotton plant is dependent.

The seed, all X 1730A cotton, is sent annually from the Gash. Planting times are irregular and are determined by the incidence and duration of the flood. Sowing is carried out immediately the land becomes sufficiently dry This may be as early as the middle of August or as late as the end of September. Planting times vary over the Tokar area more than in the Gash region because the floods are more variable and less easily controlled. Furthermore, late and unexpected flushes of the river may wash away newly planted cotton and necessitate re-sowing. The spacing of the plants is irregular: land bearing heavy weed growth or which has been only lightly flooded is planted much closer than clean, heavily watered areas.

Holes are made in the soil with sowing sticks, and the seeds are planted beneath the newly deposited and sterile silt. About a month later the plants are thinned and the weed growth may be cleaned up. On very dirty land this cleaning may consist of only the removal of the weeds in a circle around each plant, just sufficient to prevent choking. Picking may begin in early December and continue until late May or early June, and the seed cotton is sold over a long period.

(*b*) SUDAN AMERICAN AREAS

(1) **Kordofan (Nuba Mountains)**

The Nuba Mountains cover most of the Eastern and Western Jebels, two of the six political divisions of Kordofan Province. The area is from about one and a half to three thousand feet high and is composed of groups of granitic hills or jebels which rise up sharply from a more or less level plain. The hills are either of bare rock or are covered with a shallow layer of reddish-brown soil supporting short grasses and a thin growth of scrub. The soil on the flat land at the foot of the jebels is deeper, more disintegrated and darker. On the plains between the jebels the soils contain increasing amounts of clay and are of a greyer colour, but in many places there are sandy tracts formed gradually by continued deposition of material from the ever-changing seasonal streams and rivers.

The lower slopes of the jebels were formerly cultivated by the Nubas, who made a frequent practice of constructing low terraces along the contours of the hillsides to prevent soil erosion. These terraces remain in many places and some are still used for raising early crops of grain. The people live mainly on the lower hill slopes and in the valleys encompassed by hills. It is in such places that water is most plentiful and where pools, or shallow pits or wells, provide a supply throughout the year.

Agriculture now tends to be sited on the flatter lands, especially on the browner and moderately heavy clayish tracts of cotton soil, but the villages are still in or close to the hills Further away from the jebels, the heavier and greyer clays are often suitable for crops, but lack of permanent water supplies at present would prevent the harvesting of any crops grown in many such places.

The rainfall in the Nuba mountains varies from an annual average of about 24 inches in the north to about 32 inches in the south, and is quite sufficient to support a much larger population The rainy season is well defined, usually lasting from June to October Much of the rain falls in heavy thunderstorms, accompanied by strong winds, and this combination favours serious soil erosion. December, January and February are generally cool and dry, and April and May are usually the hottest months

Agricultural practices in the Nuba Mountains are generally primitive Ploughing is never practised by the natives but the soil is loosened with the aid of an iron hoe or wooden pole flattened at one end Sowing is made in July and August and later the young plants are thinned and a hoe is used for cleaning up the weeds With the exception of Government farms, there is little planned rotation of crops. Cotton growing in the Nuba Mountains has been actively encouraged since 1924, although reports make mention of earlier trials. At first cotton was usually grown on the same land for several years in succession until the soil became exhausted The ground was then allowed to revert to bush and the cultivator moved to another site, cleared it and again grew successive crops This practice of continuous cropping was also often followed for dura, the staple grain of the country, although in some places the cultivator might grow cotton for one year and dura another, according to personal whim. The picking of the crop may extend from November to January, according to the date of sowing.

A new practice known as "harig cultivation" has been spreading extensively in recent years and appears as if it will become common practice. Harig grasses are fairly tall types which grow strongly in abundance on the fertile plains of cotton soil. Following the first rains of the season the new grass and weeds immediately begin to grow Shortly afterwards the dry grass of the previous season is set alight. This old harig grass covers the ground in a dense mat, burns very strongly and so destroys the new growth and weeds. The ground is then roughly prepared and the cotton seed is sown, germination taking place following the arrival of the next rains. Two successive crops of cotton (or of dura) are usually grown and then the land is allowed to revert to harig grasses. The period under harig grass is usually two years, less frequently is it one or three. There is as yet no fixed practice and in some places there may be a first year of cotton and a second year of dura before the land reverts to harig grass

Compared with the older practice of continuous cropping this harig cultivation has the advantage that the strong growth of grass and the short period of cropping effectively help in preventing soil erosion, always a danger in lands where a moderate or heavy rainfall occurs during a short season in the year. Furthermore, cleaning of the crop is easier because many weeds have been killed off by the burning and many insect pests are reduced.

Many parts of India, with a rainfall lower than that in the Nuba Mountains, support large populations because of adequate control of their limited water supplies In Kordofan also, much use could be made of the flood waters of the many seasonal rivers which at present run to waste by petering out into the desert. In a number of places it would be possible to divert the water by a small controlled barrage and by means of canals allow it to flood evenly over large areas of good land. This "basin" type of irrigation would greatly augment the supply of sub-soil moisture, and so enable crops to be successfully carried through the dry season to give higher yields. In 1945 a scheme was started near Rahad, and the flood waters of the Abu Habl river were controlled and used for flood irrigation of the land Most of the area was used for raising much-needed grain crops, but it has been shown that good yields of cotton can be obtained.

(ii) Equatoria

Equatoria, in the extreme south of the Sudan, is the most backward province of the country It is only during the past few years that definite steps have been taken in the development of its economic resources and in the social improvement of its primitive indigenous people Cotton growing started about 1927 and steadily expanded, more particularly on the western side of the White Nile

On the east bank, cultivation was mainly centred around Torit, where a ginning factory was erected. There was also a second factory at Shukoli. The natives showed little inclination to grow cotton on an appreciable scale and the relatively small areas suitable for its cultivation gradually became exhausted. In 1942 the lack of transport and the need to grow increased food crops finally caused the Government to abandon cotton growing in this zone

In areas on the west bank of the Nile greater interest has always been displayed in raising cotton as a cash crop, although even here considerable Government persuasion was needed. The land most suitable for cotton cultivation runs along the southern border of the Sudan, in a strip some 30 to 60 miles wide It starts in the neighbourhood of Yei and stretches through

Meridi and Yambio to the district around Tambura, north of the junction of the boundaries of the Belgian Congo, French Equatorial Africa and the Sudan. This zone is about 2½-3 thousand feet above sea level and is a long-grass area of the savannah type with extensive stretches of wooded country.

The soil is mainly a grey clayish loam in a thin layer of varying depth and fertility on an underlying bed of red laterite. The rainfall in the zone suitable for cotton averages about 55 to 60 inches per annum, compared with about 40 inches on the east bank. The rains are much heavier and have a more extended season than those in the Nuba Mountains. The rainy season in Equatoria usually commences in late March or early April and may continue until November.

In the first few years following the introduction of cotton into the western zone it was grown around Yei. It was not entirely successful nor was it greatly favoured by the native cultivators. Eventually the ginnery at Yei was closed and the cultivation was extended westwards, particularly around Meridi where another ginnery was erected

A comprehensive scheme has been started to develop the Zande area, with the ultimate aim of making this stretch of country, running from, roughly, Meridi to Tambura, into a self-contained unit The plan envisages that most of the requirements of the people will be met by local production, selling products outside the area on a scale sufficiently large to raise funds for the purchase of necessities not produced locally. New cotton-growing areas have been started around Yambio and these will be extended through to Lingesi and westwards. Lingesi itself is designed to be the industrial centre of the Zande region. In addition to other local industries (extraction and manufacture of oil from cotton seed, saw mills and development of forest products), there are tentative proposals to erect a spinning and weaving mill, sufficient to meet most of the cloth requirements of Equatoria and also produce a surplus for sale in the northern and central parts of the Sudan. Should this project materialise it is expected that little cotton will be available from this region for export overseas.

When cotton was first introduced into Western Equatoria the general practice was to clear the land by burning off most of the vegetation and follow this by a little hoeing preparation Any larger scrub or trees were removed by felling or ringing Sowing was usually done in July and extended into August and sometimes September The crop was picked mainly in December and January Cotton was either grown continuously until the land was exhausted, or for two or three years and then followed by successive food crops, until exhaustion was reached. The land was then allowed to revert to bush.

Now that the area is being developed according to a more balanced scheme, attention is being given to permanent cultivation and group farms are being tried. This applies more especially to the more recently developed areas around Yambio and westwards Here holdings are being planned for cultivation on a ten-year rotation. The ground is first prepared by burning and clearing and a food crop is planted, followed by cotton in the second year and another food crop in the third year The land is then allowed to revert to bush fallow for seven years. In this way the soil is not exhausted before cropping ceases, and it is hoped to maintain the fertility by the long resting period. Soil erosion favoured by the continuous cropping of the older practice will be avoided by the shorter period of cultivation and by contour cultivation with bands of permanent vegetation between neighbour-
irrigated areas in the Sudan

One reason why cotton was first viewed unfavourably was that the picking of the crop was often as late as the end of January, or even early February, coinciding with the hunting season and the collection of wild honey. To make full use of the annual rains which commence in March, the months of April and May should be spent in preparing the ground and planting the food crops. So far as possible, cultivators are being urged to plant their cotton either at the end of May or early June. The practice of inter-cropping groundnuts with cotton is also being tried. This encourages early sowing of cotton because the cultivator naturally pays first attention to his food crops.

The earlier sowing of cotton has the advantage of making greater use of the rains and leads to the crop being picked before the end of December, thus leaving January and February free for hunting. Furthermore, the adoption of earlier sowing dates, followed by the uprooting of all old cotton sticks from the fields before the end of January, would give a close season of about four months, a valuable control measure against pink bollworm.

(iii) Upper Nile

For many years a small crop of American cotton was grown in the Upper Nile Province, on the eastern side of the White Nile from Er Renk to Malakal. During the later stages of the war the Government decided to discontinue cotton cultivation in this area and ceased issuing seed. Some small quantities were grown, presumably from seed saved by the cultivators or illicitly obtained from an outside source.

Sowing of the seed was done usually in late July, and picking started in late October or early November and extended until late January. Cultivation was primitive and crop rotation was rarely practised, cotton usually occupying the ground for four to five years followed by reversion to bush. After picking, the seed cotton was transported down the White Nile to Kosti and then by rail to Sennar for ginning at the Government factory. Unlike the rain-grown American crop from other areas, Upper Nile cotton was roller ginned.

(iv) Northern Province

The Northern Province on the borders of Egypt, has a very small rainfall and crops may only be grown satisfactorily under perennial irrigation. There are two main areas in which cotton has been grown on estates irrigated by pumps drawing water from the Nile. For many years the cotton grown in the Northern Province has been raised from American-type seed.

In the Dongola area, cotton was sown from mid-July to mid-August. In the 1939/40 season 2,000 feddans were under cultivation and grew a medium-staple type known as XA 1129. For many years pink bollworm has been a serious problem and this, coupled with acute food shortage, caused cotton to be abandoned in the later stages of the war.

Cotton was grown in the Berber area on a larger scale than at Dongola. Sowing was earlier and was usually done in May. In the 1939/40 season 2,000 feddans were grown on Government-controlled estates, from seed of two medium-staple varieties, XA. 1129 and 513. At Zeidab about 5,000 feddans of the long-staple Coker Wilds cotton was grown. Pink bollworm attack and the need for increased food production caused cotton growing to be abandoned on the Government estates. It is still practised on the Zeidab estate of the Sudan Plantations Syndicate, although even here the ravages of pink bollworm result in greatly reduced yields.

At present consideration is being given to the possibilities of re-starting cotton growing in the closed areas of the Northern Province Should this materialise, the problem of pink bollworm and choice of suitable variety will entail considerable research

II. DEVELOPMENT OF COTTON GROWING IN THE SUDAN

(*a*) Early Growth of Cotton in the Sudan

It is only during the present century that cotton has been produced on a commercial scale in the Sudan. Wild cottons have undoubtedly grown in this country since very early days, whilst semi-cultivated types have probably been raised for many years by some cultivators to satisfy small domestic needs. There is, however, little information available about such cottons Dudgeon has noted a reference by Pliny to cotton grown in the Sudan. The "Sennar tree cotton", (*Gossypium arboreum* var. *soudanense*) is a perennial native cotton of the Asiatic group. Further, as noted in the second of the present series of papers, a type of G. barbadense (*G. vitifolium,* Cavanillus) was introduced into Egypt from the Sudan and appears to have been one of the main ancestors of the Egyptian-type cottons of the present day.

The first encouragement of cotton as a major crop was given by Ahmed Mumtaz, a Turkish Governor of Suakim, who introduced it into the Tokar delta about 1850-1860. Dervish rule later interrupted the cultivation of cotton and virtually no progress was made until the Sudan Government re-started development of the country at the beginning of the present century.

From about 1900 a number of varieties of cotton were introduced from abroad, especially from Egypt Among these are noted Mitafifi, Abassi and Ashmouni By 1910 Tokar had again become important and raised the bulk of the crop, grown solely from Mitafifi seed obtained fresh each year from Egypt. The crop in the Gash delta was partly Mitafifi and partly Abassi, but a small quantity of American cotton was grown from seed brought into the country from the Italian colony of Eritrea. The Mitafifi and Nuban varieties of Egyptian cotton were grown at the Tayiba pumping station on the banks of the Blue Nile in the Gezira. Small quantities of cotton were also raised on small farms established on the banks of the Nile below Khartoum. Further north, on the Zeidab plantation in the Berber Province, Nuban and Mitafifi also formed the major portion of the crop, but several other Egyptian varieties were being tried on a small scale. Trials of American cotton (Allan's Improved and Griffiths) were also being carried out A small crop of rain-grown American cotton was being grown at this time to the south of Sennar and also in the southern parts of Kassala Province.

By now the production of cotton in the Sudan had become important and was receiving increasing encouragement A Research Farm had been started at Shambat, on the Nile below Khartoum North with the object of providing instruction for cultivators around Khartoum and in the Berber and Blue Nile Provinces. Studies were made of agricultural practices and on various crops.

In 1912 Mr. R. E. Massey was appointed as Economic Botanist and the purification of the seed supplies of the existing Egyptian strains was included in his programme. Sakel seed began to be imported in increasing amounts from Egypt. In 1912 it was grown on 200 acres at Zeidab and it quickly became apparent that this variety would soon be grown on most large irrigated areas in the Sudan.

The earlier types of Egyptian cotton were discarded and Massey mainly concentrated upon selection work from Sakel stock to provide a more satisfactory main Egyptian-type crop He also carried out a considerable amount of work on American cotton, which was increasingly favoured for growth on the northern pump schemes on the Nile, using as his material seed of a large number of varieties imported from the U S.A.

(*b*) DEVELOPMENT OF THE PRESENT SUDAN SAKEL CROP.

Until comparatively few years ago fresh Sakel seed was imported at intervals into the Sudan. Only since the decline of Sakel in Egypt has the Sudan relied solely upon her own resources for the production of planting seed and for the maintenance of lint quality. The Research Division of the Department of Agriculture and Forests maintains a large breeding programme for developing strains more suited to Sudan conditions.

A strain known as Massey's Selected Domains Sakel originated from Sakel seed imported in 1922 This strain has been grown experimentally for many years as a standard variety for use in long term agronomic experiments on the Gezira Research Farm.

Another selection made about this time is that known as Sakel 186. A. R. Lambert took this strain as a basis and started to make re-selections. After the opening of the Sennar Dam, and the first big extension of the irrigated area in the Gezira in 1925, M. A Bailey was appointed as the first full-time plant breeder to free Massey for work on blackarm and other diseases. He continued work on Sakel 186, and by 1930 the re-selections of this strain had been shown to be somewhat superior to other Sakel types. Consideration was being given to replacing the main-crop ordinary Sakel in the Gezira by the re-selected Sakel 186 Much promising work had also been carried out on hybrids between Sakel and Sea Island

A new feature now appeared in Sudan agriculture and completely altered the picture Leaf curl first appeared on an appreciable scale in the 1924/25 season, and this disease spread rapidly until in the 1928/29 season there was general infection throughout the Gezira. Sakel 186 was as susceptible to this disease as the ordinary main-crop Sakel and consequently its bulk propagation was no longer continued. Most of the Sakel × Sea Island hybrids were also susceptible and consequently discarded The urgent problem in the breeding programme was to develop a new leaf-curl resistant cotton.

In 1923/24 Lambert made a number of selections from Sakel 186 with the object of developing resistance to blackarm disease. Some of these families were passed on to Bailey and were grown at Shambat in the 1928/29 season when it was found under Gezira conditions some showed resistance to leaf curl Further selection led to the choice of the two strains X 1530 and X 1730 in the 1929/30 season Compared with Domains Sakel these types were of a more bushy habit, somewhat later fruiting and had the capacity to recover and grow away from an early attack of blackarm, although not possessing true resistance to the disease.

Small-scale trials were made in 1932/33 in various parts of the Gezira and these showed that the new strains were better in yield than Domains Sakel. In 1930/31 selections X 1530A and X 1730A were derived and these subsequently proved superior to the parent stocks. By 1933/34 seed of these selections was being increased at the Barakat Seed Farm of the Sudan Plantations Syndicate

Meanwhile seed of the X 1530 type had been issued for bulk cultivation and was being grown on a wide scale by 1934. It was followed by the later X 1730A type (the original X 1730 was never issued for bulk growth) which showed itself to be more satisfactory. The X 1530 type of cotton was gradually displaced by X 1730A, being grown in the Gezira for the last time in the 1938/39 season, but some persisted in the Tokar area for a little longer.

A third Sakel type, known generally as NT 2, originated from a single plant selection made in the 1929/30 season from Gash Sakel in the Gash Delta. Shortly afterwards it was recognised that the X 1530 and X 1730 families were of coarser fibre than typical Domains Sakel. Workers in the Sudan of the Research Division of the Department of Agriculture and Forestry found the NT 2 selection to be resistant to leaf curl disease and this characteristic was improved by further selection work in order to obtain a high quality resistant cotton of true Sakel type In the 1944/45 season two strains of NT 2 were being grown in small quantities to gain the reactions of spinners to this class of cotton. The NT 2/36 was the standard type and the small Gezira crop of this cotton appeared on the market under the GN series of marks. NT 2/41 was the second strain, obtained by adding blackarm resistance to the sub-strain NT 2/38, and was grown in the Gash on a small scale, being marketed as "Barsak". Further small quantities of NT 2 cotton were raised in the next season when it was decided to discontinue further propagation of this class of cotton. NT 2 generally gives yields fully as good or slightly better than Domains Sakel, but it is of somewhat coarser fibre and lower yarn strength. There appears to be no firm demand for a cotton with a quality between that of standard Domains Sakel and X 1730A.

Intensive breeding work on the present crop of Sudan Sakel, of X 1730A and Domains types, is in progress in the Sudan. The various aspects of this work, and the classification and characteristics of the commercial crop, are described in later sections of this paper.

(c) DEVELOPMENT OF THE PRESENT SUDAN AMERICAN CROP.

In section (i) above, mention has been made of the growth of American cotton in the Sudan prior to 1913 There are reports in 1913 of trials of Sunflower, Nyasaland Upland and other types of imported American cotton on pump schemes along the banks of the Nile in the Northern Province. In 1914 a Nyasaland Upland type was being grown at Zeidab and on various Berber estates. By 1925 the strain of Sudan American known as "Pump Scheme Strain" was well established and it appears probable that it was derived main from Nyasaland Upland. Between 1913 and 1925 various introductions from America continued to be made, but none of these proved as satisfactory as Pump Scheme Strain. The adaptability of Pump Scheme Strain may be due to the mixture of varying plant types in the crop which enabled it to settle down in different environments. Work on the various imported strains showed little promise of breeding a superior yielding type, and gradually the attention of the cotton breeders was devoted to other cottons of higher quality lint or earlier maturing habit.

Delta Webber seed was imported from America and was grown on some pump schemes in the Berber area A selection of this cotton, Delrect I, reached the commercial stage but never found great favour. The Zeidab estate of the Sudan Plantations Syndicate imported the long-staple Coker Wilds strain from America. This type (strain Wilds No. 11) has now given place to Wilds No. 16 S.C which is still grown there, and is the highest quality American cotton produced in Africa. Although grown under irrigated conditions, it does not give high yields, mainly because of attack by pink bollworm and a capsid (*Creon tiades*).

Among the somewhat longer staple cottons introduced from America was Meade which for a number of years formed the basis of part of the breeding programme. The strain known as XA 1129 was derived in the Sudan from the selection of a single off-type plant found in a plot of Meade. Under irrigated conditions XA 1129 was earlier cropping than the Pump Scheme Strain and of higher ginning out-turn, and its better lint quality resulted in a higher cash return per acre Eventually XA 1129 was widely grown in the Dongola district and continued as the main commercial type until cotton growing ceased there in 1942 It was also introduced into the Government controlled estates in the Berber district

The Berber district generally suffers more from pink bollworm attack than the Dongola area. An earlier maturing type than Pump Scheme Strain or XA 1129 was found to be essential in order to permit the picking of a reasonable crop before destruction by pink bollworm. About 1933 the cultivators were prepared to abandon cotton growing but fortunately a partial solution was found The "Punjab Early Strain" of American cotton had been introduced previously from India and experimental trials had been made. The strain known as "513" was derived from Punjab Early Strain and proved to be particularly early maturing. Seed was multiplied and issued to cultivators. It soon became popular and gave yields up to twice those of later maturing types By 1936, strain 513 was the main commercial variety on the Berber estates other than Zeidab. The growth of 513 and XA 1129 continued in this area until cotton growing was abandoned in 1942.

When the rain-growing areas began to be developed, breeders found the Pump Scheme Strain to be the most suitable variety for the new wide range of conditions. It was grown generally in the Upper Nile Province and, after being introduced into the Nuba Mountains in 1924, it has always formed the bulk of the Kordofan crop Small amounts of the American variety Deltapine (described later) were raised in the 1944 season in the Kadugli district. Although this cotton gave better yields than Pump Scheme Strain it is of lower quality and its propagation has been stopped so as not to lower the reputation of Sudan American cotton.

Between 1925 and 1936 many varieties and re-selections of American cotton were subjected to trials in the Nuba Mountains but gave no marked increase in yield over the Pump Scheme Strain. In the 1936/37 season the breeding of American types was transferred from Shambat to Kadugli The breeding strains for irrigated conditions was virtually abandoned and work was focussed almost solely upon cottons suitable for Kordofan and Equatoria. The change in agricultural practices in the Nuba Mountains has given rise to new problems As mentioned in Section I of this paper, earliness of growth is now an essential requirement in any cotton chosen for commercial production in the Nuba Mountains and unless an early strain is issued to the cultivators poor crops will be obtained in seasons when the rains are delayed.

Plant breeders have developed two strains of cotton, BAR SP 84 and NT 205/43 which are of early maturing habit compared with Pump Scheme Strain It appears probable that BAR.SP 84 will replace Pump Scheme Strain and become the general variety for growths in this area.

In Equatoria also the Pump Scheme Strain was chosen for propagation when cotton growing was first started. The strain XA. 129, a selection of Pump Scheme Strain was found to give somewhat higher yields and became the commercial variety in districts on the eastern side of the Nile until cotton growing was abandoned there. In areas on the western bank the strains known as 511C and 511D (described in Section VI (*a*)) displaced the Pump Scheme Strain. The later selection 511D has continued to be grown but the BAR SP 84 from the Nuba Mountains has been chosen for the newly opened districts around Yambio. BAR.SP.84 has given equal to slightly better yields than 511D in variety trials and it is possible that it may also become the standard variety in the present main area around Mendi.

III. DISEASE AND INSECT PESTS

A comprehensive understanding of the problems of a cotton-growing area is impossible without some knowledge of the reasons for loss of crop and for decline in cotton quality. This section is devoted to a general account of the work of The Research Division on the cause, effects and control of the more important disease and insect pests which injuriously affect cotton in the Sudan Breeding work directed towards developing particular immune or resistant strains is not described in this section but is considered in later portions of the paper.

(1) DISEASES OF THE COTTON PLANT.

In the Sudan the cotton plant is liable to suffer from a number of fungal, virus and bacterial diseases. Among these that known as "black-arm" is very serious, "leaf curl" has given great trouble in the past but is now partly conquered, and "cotton wilt" is sometimes a source of crop loss.

Blackarm

This disease is caused by a bacterium (*Bacterium malvacearum*). In Egypt it is manifested by the symptoms of "angular leaf spot", but in the Sudan a more severe form occurs which may attack the main stem, branches and bolls as well as the leaves of the plant, and result in heavy loss of crop. The following account is based mainly on articles written by Massey and Knight on their work in this field

Attack of the leaves can occur if the surface is wetted and a continuous film of moisture exists, within which the bacterium may be drawn through the stomata into the interior tissue. Should the leaf be dry, the organisms can remain dormant on the surface for a long time until conditions favourable for their entry into the sub-stomatal cavities arise. Leaves with only a moderate degree of attack show small reddish brown lesions between the veins and many of these assume an angular shape In the more severe forms of attack the tissue lesions become larger and coalesce, vein lesions also develop. The large lesions are wet and when the attacked tissue dies it turns black as compared with a brownish colour in the milder forms.

The loss of vitality due to the withering and shedding of attacked leaves is sufficient in itself to result in a decline in yield. Heavy loss also arises from other manifestations of the disease. Infection of the main stem may result from the direct penetration of the bacterium into healthy tissue, although under conditions prevailing in the Sudan it frequently occurs *via* the petiole following leaf attack Large water-soaked lesions occur and if attack is severe the stem may be girdled and break Side branches also may be girdled and break off, causing partial loss of the crop

Later in the season the bolls themselves may be attacked, either by spread of the disease along a blackened arm or stalk, or through rain splashes from diseased leaves and debris The first appearance of blackarm disease on the boll shows as water-soaked areas which gradually spread and these diseased portions turn brown. Especially when attacked in an early stage of development, the bolls frequently dry up, become prematurely hard and may split open at the top or along the side. Very early attack may result in a complete cessation of development due to rapid spread of the disease, whilst the splitting open of older and less severely attacked bolls results in the lint becoming exposed, stained and matted.

The disease only appears to be spread in association with water, one of the main sources of carry-over being the infection on the seed coat and fuzz. Dry infected matter lying dormant may be activated by heavy dew, and infection may also take place by contact under humid conditions. More particularly, however, the disease is spread rapidly by heavy rain-storms accompanied by strong driving winds

The persistence of blackarm, and the degree of infection of the new crop in the next season, depend greatly upon the magnitude of carry-over of the disease. In the field the disease survives because dry woody tissue can retain the organism in a viable condition for a long period. Ground littered with debris, ratoons, and young seedlings from infected seeds all favour the spread of the disease, particularly since cotton may be grown on adjacent fields in two successive seasons The high incidence of blackarm in the Gezira primarily arises from the climatic conditions. In the close season the weather is dry and there is only very slow destruction of field debris. Moreover at planting time the soil temperature is favourable for the development of seed infection. Prolonged immersion in water renders any infected tissues innocuous and consequently in the flood irrigation areas of Gash and Tokar the carry-over of the disease in the field is on a much smaller scale. In these two areas the climatic conditions do not greatly favour the infection of the young growing crop with blackarm. Chilling of the soil by rain during the germination stage is believed to lead to increased seed infection and in Tokar the absence of rain prevents any spread of blackarm. In the American cotton growing areas of Kordofan and Equatoria, a large amount of the field debris rots away in the close season. Blackarm disease in these rain-growing areas does not present such a formidable problem as in the irrigated regions

Another cause of the persistence of the disease is infected dust in ginneries which contaminates the planting seed. Furthermore some of the seed itself may have been originally infected following boll attack Seed infection may persist for as long as two years, and may result in infection of clean seed because the disease is contagious

A number of measures are in force to control blackarm disease. The destruction of old plants at the end of the harvest is practised to keep down pink bollworm, and this measure is also an effective help in reducing the carry-over of blackarm disease In the Gezira a further precaution is taken of gathering and burning the leaf and twig debris in the fields In some blocks, where infection has been high during the season, the ground is flooded for a few days to render innocuous any debris which has been overlooked

The Gash area is used for large-scale seed multiplication because of its greater freedom from blackarm disease. It is planted with disinfected seed sent from the Barakat Seed Farm; the multiplied seed is then disinfected and used for the planting of the Gezira area in the following season.

The above measures have been successful in keeping the disease in check, but there is always the possibility that severe outbreaks may occur. Consequently the attention of research workers has been concentrated on the urgent problem of developing strains of cotton having adequate resistance to blackarm disease. At an early stage Knight and Clouston (see Section VII (*a*) showed that resistant strains of cotton could be developed, but there remained the more difficult task of synthesising strains in which the resistance to the disease was added to the desirable agricultural, fibre and yarn characteristics of the present strains of Sudan Sakel. In view of the importance of this problem a more detailed discussion of the work by Knight is given later in the paper.

Leaf Curl

This is a virus disease which constitutes a potential danger in the Egyptian cotton areas in the Sudan The first sign of the disease is a local thickening of the veins on the under side of the leaf, or on the leafy bracts This may easily be detected by holding the leaves up against the sunlight when the veins appear opaque. This thickening gradually extends and the leaf begins to curl or crumple up. In extreme cases of attack the main stem, the fruiting branches and the leaf stalks assume tortuous shapes The effect is often partial or complete sterility of infected parts of the plant, resulting in marked loss in yield.

From the work described by Massey and Andrews, leaf curl does not appear to be transmitted by seed infection, but is spread by white flies, which feed on the leaves of affected plants, and then pass on the disease when they transfer themselves to healthy plants and again commence feeding. The disease is kept in check by the close season, during which period there are few weeds or food crops. The main source of re-infection is in infected ratoons, shoots springing up from old tap roots or old stumps left over from the previous season. To reduce this to a minimum tools were devised for pulling up all plants by the roots after the end of the harvest instead of cutting them down as in the older practice Although rigorous uprooting of old plants is now carried out, a few plants nevertheless break at ground level and may spring up again in the following season, in numbers sufficient to cause a fresh wave of infection.

Bamia acts as a host to leaf curl disease, but its growth is prohibited in the close season, as a preventive measure against pink bollworm, and this practice also serves as a control measure for leaf curl As a further help, the leaf-curl resistant Momtaza bamia is being encouraged in preference to the local type.

The greatest prospect of avoiding crop loss from leaf curl lies in the development of resistant varieties. As described later in this paper, the X 1730A variety was developed in the Sudan on account of its being resistant to this disease Further breeding work is in progress to render Domains Sakel resistant to this disease without in any way affecting its fibre quality.

Cotton Wilt.

One form of this disease, caused by the attack of the root system of the plant by a fungal parasite (*Fusarium vasinfectum*) living in the soil, has been described in Part II of the present series of papers Typical signs of attack are the dropping of leaves after mottling and yellowing, possibly followed in extreme cases by the plants wilting and dying. In Egypt the effects of this disease are serious and it has been necessary to develop immune or resistant strains. In the Sudan, however, there are rarely serious outbreaks; the disease does not appear to be spreading and no active counter measures have as yet been required.

(ii) INSECT PESTS OF THE COTTON PLANT

In the Sudan, as in most cotton growing countries, there is a wide range of insects which attack the crop Some cause damage immediately the seed begins to sprout, whilst others manifest themselves as the crop approaches harvesting. The more important among them are considered below.

Pink Bollworm

For many years pink bollworm (*Platyedra gossypiella*) has been one of the major cotton problems in Egypt from whence the pest appears to have spread into the Sudan. Pink bollworm in the Sudan is mainly prevalent in the irrigated areas; in the rain-growing areas of Kordofan and Equatoria it usually gives little trouble. The Tokar and Gash crops are frequently threatened, and the Gezira to a less extent. But for strict control measures there would be a heavy annual toll on the crops in these regions. At Zeidab, pink bollworm caused a marked loss in yield and investigations are in progress to see how far this may be reduced.

In Part II of the present series of papers was given a brief description of the pink bollworm, its habits and mode of carry-over from one season to the next. Crop loss results from the shedding of bolls attacked during early stages of development, and also by the partial destruction of the contents of older bolls. The remaining contents of such older attacked bolls are composed of immature, weak, short lint which reduces the average quality of the cotton

Many of the control measures against pink bollworm in the Sudan are similar to those in force in Egypt. The seed for the Gezira is treated at Meringan by the Simon Heater and dusted with Abavit B at the same time. Legislation provides for the collecting and burning of the old cotton sticks left after picking in order to ensure an effective close season The earliest date of sowing, and the latest date for the destruction of the remains of the old crop are fixed annually for each district. Permission is also required before seed may be moved from one area to another, and quarantine regulations apply to the import of seed from abroad. The prohibition of bamia, an alternative host for pink bollworm, during the close cotton season, has already been mentioned

In a later section of this paper, reference is made to recent developments in the breeding of varieties resistant to pink bollworm.

Locusts

These provide another serious pest problem in the Sudan Both cotton and other crops are frequently threatened by swarms which have either invaded the country or have bred on a large scale within the Sudan. The damage varies from year to year, and the number of swarms fluctuates annually in an irregular cyclic manner

There are several kinds of locusts which give trouble but the two major types are the Desert Locust and the Tropical Migratory Locust Locust eggs are laid in moist soil After hatching, the nymph comes up to the surface, casts its skin and appears as a wingless locust, usually termed a hopper During the next month or two, the hopper grows, sheds its skin at intervals and eventually turns into a winged adult.

Early immigrant swarms appearing in May and June usually cause little harm because there are few crops growing at that time After these swarms have passed through their breeding stage, severe damage may occur if the hoppers invade growing crops, but most of the harm is caused by young winged adult locusts during September and October when emigration takes place

It is difficult, and indeed almost impossible, to counter flying swarms. The most effective control is gained by combating locusts in the hopper stage. Hoppers are usually killed by the use of poison bait, a mixture of bran, molasses, sodium arsenite and water A large number of scouts are posted to report on all swarms and their movements, and on the whereabouts of the breeding grounds Dumps of bait are maintained in readiness all over the country with reserves at district control centres Information is sent in by scouts to a central control point, which also receives reports regarding locust swarms from other countries also concerned with the locust problem. Paid labour is used to fight the numerous outbreaks of hoppers which occur each season, and is recruited locally A permanent supervisory staff is also maintained and in many cases transport has to be hurriedly arranged to bring further supplies of labour and bait to severely threatened areas If the hoppers are successfully tackled, few adult swarms occur and little damage ensues.

Jassids or Cotton Leaf Hoppers

Cotton suffers from the attacks of jassids (*Empoasca libyca*) in many parts of the world. In the Sudan jassids have become an increasingly severe problem since about 1930 They appear to be increasing in the Gezira, particularly in the northern parts, and serious attention is being given to developing efficient control measures.

The jassid has a short egg and nymph stage and a relatively long adult life. The eggs are not laid in a few large batches but in small numbers at frequent intervals over a long period. The nymphs feed on the leaves of the cotton plant which then begin to dry up from the edge, assume a crinkled form, and then eventually wither. The result is a marked reduction in the general vitality of the plant.

In the Sudan the particular species of jassids prevalent have a wide range of host plants. Consequently the close cotton season does not provide an effective means of control. Spraying the crop with Bordeaux mixture has been tried since 1941/42, more especially in the north of the Gezira Increases in yield, up to ten per cent , have resulted from the spraying of crops and the figures give some general indications of the magnitude of the loss which jassids cause The use of DDT sprayed in emulsion form is also being tried This insecticide appears to give effective protection to the leaves for about a month Improved yields have been obtained following spraying with DDT, the increase being mainly due to heavier later pickings rather than a general increase from the first picking onwards Over an area of 40,000 feddans increases in the region of 40 per cent were obtained

Although effective control of jassid by some form of spraying now appears to be feasible, there is the disadvantage that any such method is extremely costly, not only in material but more especially on account of the large-scale use of labour and equipment entailed Consequently research is in progress in the Sudan to see whether resistance to jassid attack may be transferred to Sakel from other cottons. A more detailed discussion of this aspect is given in a later section of this paper.

Cotton Thrips

Irrigated crops of cotton in the Sudan suffer from attack by thrips (*Hercothrips* spp.). In the Gezira the thrips are more prevalent in the south than in the north, and in some seasons may cause appreciable loss. Rain-growing areas are generally free from this trouble, particularly the Nuba Mountain area of Kordofan where thrips do not appear to constitute any serious danger.

The eggs are laid inside the leaf tissue, generally on the lower surface. The larvæ which hatch out from the eggs, and also the adult thrips, feed on the plant sap, causing a typical browning and silvering of infested leaves followed by withering and leaf fall The fully grown larvæ fall to the ground and pupate, remaining in the soil for a variable period, from less than a week to more than a month, according to prevailing conditions As a result of the short pupation period, successive broods of thrips gradually move up the plant to higher and newer leaves as the lower ones become exhausted If infestation is severe, the stem, bracts and bolls may suffer from direct attack as well as the leaves This causes boll shedding and consequent loss in yield. The loss of a large number of leaves also induces boll shedding since the reduced vitality of the plant prevents it from carrying all of its crop

Frequent irrigation appears to seal up the pupæ in the ground and reduces the reproductive rate Thrips are mainly active about October and November and at this time the plants have grown sufficiently to withstand frequent waterings with few subsequent ill effects. As a result of experimentation the watering interval is shortened when thrip attack takes place The use of insecticides on a large scale against thrips alone is rarely economic, but should DDT spraying against jassids become general, then the crop loss caused by thrips would be reduced because this insecticide also kills off the larvæ of the thrips immediately after hatching

Cotton Stainer-Bug

The distribution of cotton stainers (*Dysdercus* spp) is greatly dependent upon rainfall and these insects only become plentiful in places where the annual precipitation exceeds about 20 inches. Consequently stainers are not a pest affecting the irrigated cotton crops in the Sudan but only cause damage to the rain-grown American types in Equatoria and Kordofan.

Stainers obtain their main nourishment from the seeds of a limited number of species, although this is frequently supplemented by the saps and nectars of various plants The nymphs have a very long proboscis and use this for piercing and sucking unripe seeds in their cases In cotton the damage is not immediately apparent until the boll ripens and opens, when it is seen that it contains a mass of stained lint This staining is not caused by the stainer-bug itself, but by the development of bacteria and fungi which have been introduced into the boll case by the proboscis of the nymph In addition to the yellowish staining there is also damage to the seeds which frequently produce only a small amount of immature, worthless fibre. Fungal attack ceases after the boll splits open but the lint may become more stained by the excreta from the insects.

In the Nuba Mountains *D fasciatus* is the stainer which causes most damage. Breeding of this bug continues throughout the year, is highest during the rainy period, and is greatly retarded in the hot dry season Large colonies of the insects accumulate on the bark of *tebeldi* trees After the fruit of these trees has fallen the seeds in the capsules are exposed and eaten by the stainers. Breeding is rapid and the pest then disperses to settle on cotton crops Control is applied by locating all tebeldi trees within a few miles of the cotton area, not very difficult since there is not a large number of them and they grow mainly near hills or on high ground. The trees may be sprayed twice a year with paraffin and then ignited, which kills the pest but only retards the tree The early removal of cotton sticks, and the prevention of hoarding seed not required for sowing, is a further aid The effective application of these measures, and the planting of cotton on land removed from the tebeldi trees, will keep damage by stainer down to a low proportion.

In Equatoria *D. superstitiosus* is the species which gives rise to most troubles and in some years and localities may cause very serious damage. There is no pronounced dry season in this part of the country and the rainfall is much heavier than in Kordofan. Breeding goes on throughout most of the year and makes control very difficult The hand-picking of insects in the field has been tried and if repeated at frequent intervals this practice is satisfactory On the other hand, as might be expected, such a method finds little favour with the native cultivators

Miscellaneous

Egyptian bollworm (*Erias insulana*) and Sudan or Red bollworm (*Diparopsis castanea*) also occur and do damage, though on a much smaller scale than Pink bollworm. American bollworm (*Heliothis armigera*) is ever-present in Kordofan and doubtless causes some damage, but on a much smaller scale than the other bollworms

Lygus appears in Equatoria but its effects here do not seem to be so pronounced as in the cotton growing areas of Uganda to the south-east. Cotton leaf rollers (*Sylepta* spp) also occasionally cause damage, in some areas Young plants are often attacked by termites (white ants) and flea-beetle (*Podagrica puncticollis*), the magnitude of the attack varying from season to season.

Cotton aphis or green fly is often troublesome. This insect attacks the plants by inserting a long proboscis into the cell tissues and withdrawing the sap. Aphis excretes a sweet, sticky substance known as honeydew, which adheres to the leaves and blocks up their pores, thus preventing them from carrying out their normal functions In the Gash, cotton aphis causes serious damage in some seasons.

Helopeltis bergrothi are sucking insects and can cause several types of damage to the cotton plant The main stem may receive lesions at an early stage in the development of the plant and so suffer severe stunting and malformation. Larger plants may have their branches and buds attacked Later in the season the green bolls are attacked and show typical "cratering" on the surface caused by the insects feeding on the carpel tissues This cratering often results in abortion or premature opening and may be followed by invasion of secondary pests resulting in total loss of the boll Incidence of *Helopeltis* in cotton areas is usually erratic and generally areas of low rainfall experience little or no trouble Equatoria is the only area where severe damage occurs, and this only in some seasons So far no effective means of control are known

IV. MARKETING AND GRADING

After the cotton has been picked by the cultivator it is taken in sacks to the ginnery where it is graded and payment made according to weight and quality. The methods of grading vary for the different types of cotton and, in some cases, in different areas growing the same type of cotton A general description is given of the various methods of grading in the Sudan Sakel regions followed by a brief account of the current practice for the American-type crop

(*a*) SUDAN SAKEL

(i) Gezira

Cotton grown in areas watered by the main irrigation scheme depending on the Sennar Dam is brought to one of two main ginning centres. One group of ginning factories is at Hasiheisa and serves the northern parts of the area under the control of the Sudan Plantations Syndicate, the whole of the Kassala Cotton Company concession and also the Abdel Magid Scheme. The ginneries at Maringan, near Barakat, are used for the crop grown on the southern parts of the Sudan Plantations Syndicate's concession.

In the Gezira, pickings are made steadily throughout the season and cultivators are encouraged to bring their seed cotton to the ginnery as soon as possible. The large number of pickings results in cotton coming forward in a steady flow. Seed cotton reaches the ginnery packed in bags bearing the block number of the land on which it has been grown and also the number of the tenant's holding Each bag, which holds about 100 lb., is weighed and then assessed separately by a seed cotton classifier.

The Sudan Plantations Syndicate have on their staff a chief cotton classifier who is usually stationed at Port Sudan. At the beginning of each season he visits the factories at Barakat and Hasiheisa and examines samples of ginned lint which have been previously graded as seed cotton by the usual staff of classifiers These lint samples of the new crop are then compared with reference samples of lint cotton of corresponding grade of the previous season If any consistent differences are noted the seed cotton classifiers adjust their standards until they conform with those of the previous season. The chief cotton classifier stays until satisfied that classifiers are working on the same basis as that of the previous year. This practice ensures that each individual seed cotton classifier works to a common standard and that there is continuity in the level of classification from one season to another.

Bales of cotton grown on the concession of the Sudan Plantations Syndicate are distinguished by the letters GS (for the Domains Sakel type) and GL (for the X 1730A type) together with a number denoting the grade and also a bale lot number. The cotton grown under the supervision of the Kassala Cotton Company is similarly labelled but each bale also carries the symbol KCC. Bales of cotton from the Abdel Magid scheme are marked AM (Domains Sakel) or AL (X 1730A) in place of the GS and GL markings of the main Gezira crop

There are six full grades, 1-6, and also half grades denoted by X (extra). Thus XG4S is extra grade 4 Domains Sakel type, midway between G3S and G4S

A classifier judges seed cotton according to his observations on various factors which are considered to affect the quality and value of the cotton One of his problems is to make reliable and rapid observations: having done that he then has another task A cotton may be ranked high on account of some features and low on account of others. The classifier has to arrive at a single figure—the grade category—which sums up his combined impression of the several different characters observed. Consequently a given grade of cotton cannot be composed wholly of bales of cotton of identical quality There is a permissible range of variation in the different characters, outstandingly good qualities in some directions being counter-balanced by poorer qualities in others The various factors determining grade are considered below

The rapid classification of each sack of seed cotton brought into a ginnery necessitates the seed cotton classifier observing almost subconsciously, by hand and by eye, a number of widely different features. He does not determine the length of staple by "pulling" to form a tuft (that is only done on bale cotton in the later examination at Port Sudan) but bases his judgment upon the manner in which the seed cotton clings or drags when a handful is drawn apart Increased length of staple tends to raise the grade, shorter staple lowers the grade. Fibre fineness is noted mainly by feel but partly by appearance. Immature cotton tends to reduce the grade and is noted by observations on lustre and feel, and by a "cloudy" appearance of the lint. Increased proportions of stained cotton generally caused by insect attack result in a sample being given a lower grade than one with little stain. Greater importance is given to stain than to many of the other features, since a stained sample is usually an indication that staple and maturity have been adversely affected during growth. Freedom from leaf and trash is also observed but in the Gezira the importance attached to this feature is not so marked as in some of the other areas. The grade of the Gezira crop tends to fall off steadily as the pickings progress in the season, and it is recognised that the higher grades of cotton should contain smaller proportions of trash than those of lower grade. Sometimes a cotton might be classified as of high grade but for its having a trash content higher than is usual for that particular grade, and these cases are treated separately. The sacks of seed cotton are classed as high grade but are specially marked, the seed cotton being given a light mechanical cleaning prior to ginning in order to reduce the trash content to a figure normal for that grade.

Each ginning factory contains a double set of 40 roller gins, with a baling press at each end Only one grade of cotton is ginned at a time, and material from several sacks, possibly coming from different lots, is sprinkled with water and fed into the gins. As the cotton comes through the gins it is well mixed before being placed in the baling press This practice results in reducing the possibility of marked differences in quality occurring in different bales of the same mark.

The regular flow of cotton from the field to the ginnery in the Gezira is a great aid in grading The first picks tend to be of grades 1 and 2, followed by successively lower grades as the season progresses. The work of the seed cotton classifier is thus rendered less difficult than if sacks of cotton of all grades came forward at the same time

The bales are sent by rail to Port Sudan for shipment overseas, arranged in lots containing up to 500 bales of the same grade At Port Sudan a further examination is made of the cotton as a check on the seed cotton grading. The chief cotton classifier samples a number of bales in each lot and compares them with his standard samples of the previous season to ensure that the quality is fully representative In nearly all cases his judgment confirms the original classification, although at times he may differ and cause a lot to be either raised or lowered half a grade

Cotton from the White Nile Alternative Livelihood Schemes and from the private estate of the Mahdi is graded and ginned at the Government ginnery at Sennar The description of the grades is the same as in the main Gezira scheme, with full grades running down from 1 to 6, and the symbol X being used with a number to denote a half grade higher. Only Domains Sakel is at present grown in the various White Nile Schemes and bales of it are marked WN. Domains Sakel cotton from the Mahdi area is marked MS, and X 1730A cotton bears the symbol ML.

The ginnery at Sennar has to serve a number of small areas which together form the White Nile Scheme. Consequently there is no steady flow of pickings nor consistent decline in cotton quality as the season progresses. The grading system is not standardised or checked against the main Gezira system At Sennar assessment of grade depends almost exclusively upon leaf and stain and little upon fibre characteristics. Consequently, as shown later in this paper, it is not surprising to find material differences in quality between samples of the same grade coming from these two areas

(ii) **Gash**

The production, grading and marketing of the Gash crop is under direct Government control. When the picking season approaches, the Inspector of Agriculture sees that each tenant is issued with a number of sacks in which to place the seed cotton as it is picked. The sacks are labelled according to the type of seed sown (Domains Sakel or X 1730A), with the number of the tenant's holding and with the type of infection from blackarm disease This latter information, whether the crop has received light, heavy or no infection, is added for purpose of control of planting seed in the next season. The cultivators bring the sacks to different centres along the railway line, where they are sorted for type When a sufficient number have accumulated they are transported to the Government ginning factory at Port Sudan. At the ginnery the sacks of seed cotton are stacked, cotton from each district being kept separate.

The seed cotton is graded before ginning, each sack being opened at the mouth to permit the withdrawal of a sample. Unlike the Gezira there is no marked, consistent variation in staple length over most of the season nor is there a regular succession of different pickings arriving at the ginnery. Because of variation in the date of sowing and in growing conditions, a given lot of cotton may be composed partly from the early crop, and partly from the later crop. Consequently, in determining the grade of a given sack of seed cotton, no attention is paid to the question of staple length. The only factors considered are the proportions of trash and of stained cotton. As distinct from the Gezira, there are no half grades in use in the Gash, the six full grades running from 1 at the top of the scale to 6 at the lower end. Added to the grade number is a K to denote the origin and S or L according to variety. Thus K3S or KSSS is third grade Gash Sakel of the Domains type, K5L is fifth grade Kassala Sakel of the X 1730A variety.

Each lot of Gash Sakel is composed of about 200 bales, all of the same grade and from the same district. Careful mixing is carried out in the ginnery to reduce the bale to bale variation within a given lot of cotton Since, however, staple length is not considered in grading, and also because bales from districts are not mixed together, it may be found that the average staple of one lot of bales may differ appreciably from that of another lot of the same mark from a different district where growing conditions are not similar. The trash content and the proportion of stained cotton in the two lots would of course be similar

The ginning factory at Port Sudan is run in two different sections, Domains Sakel being ginned in one half and X 1730A in the other. This practice was established to minimise the risk of admixture of lint, or of seed of the two varieties. The factory also gins part of the Tokar crop, and this cotton is used as a "balancer". When sufficient supplies of one of the two Gash types are not forthcoming, the portion of the factory devoted to that variety is completely cleaned. Supplies of cotton from the Tokar area are then ginned until stocks of Gash Sakel have again accumulated.

(iii) Tokar

Planting times in Tokar are irregular because of the dependence upon the annual flood, and consequently pickings are spread over a long season. At one time a given district may be picking early cotton and another may be picking late cotton.

The free marketing of cotton in Tokar was restricted both during and following the war, although control of the crop has never been as strict as in the Gezira or the Gash area Buyers travel over the Tokar region and buy seed cotton from individual cultivators, many having their customers scattered over the whole of the Baraka Delta. After the buyers have purchased the sacks of seed cotton, these are brought into Tokar where they are opened and classified by a Government grader.

As in the Gash, the grading of the Tokar crop is based solely upon visible characteristics, the amount of leaf and stained lint being the determining factors. In some cases lustre may also be given secondary consideration in determining whether a given sack should be classified as the highest grade. There are five recognised full grades in the Tokar system, but in recent years only the first four of these have been effective. There has been an increasing tendency to ignore completely the fifth grade. Since only one variety of cotton is grown in this area, the X 1730A type, there is no need to have a varietal mark The Tokar grades run from T1C to T4C, or to T5C if this should be used. As may be seen from this classification, the Tokar grading system is not standardised against that of the Gash or the Gezira. About 70 per cent of the crop is classed as Grade 1, partly because of the relatively uniform climatic and moisture conditions over most of the crop season and partly because of the standard of classification Grade 1 in Tokar covers a wider range of quantity than in the Gash—much of it is not equal to Grade 2 Gash L cotton (K2L). Some reorganisation of grade classification in Tokar would be welcomed by many consumers Certainly any grade, like T1C, which covers nearly three-quarters of a crop is too broad.

After grading, the bags of seed cotton are re-allocated to several main buyers. By official arrangement, the seed cotton allocated to some of the buyers is sent for ginning to the Government factory at Port Sudan. The larger portion of the crop, usually 75 per cent of the total, is ginned at a privately-owned factory at the port of Suakin on the Red Sea coast some 55 miles from Tokar.

Because of the method of purchasing, the bales in a given lot may contain cotton from not only different pickings but also from districts widely apart. The cotton varies somewhat in staple length as the season progresses and according to the conditions in the different districts Consequently not only may lots of the same grade differ in average staple length, but also there may be marked variation in staple (and other characteristics) between bales in the same lot.

(*b*) SUDAN AMERICAN.

(i) Rain-Grown Cotton

Because the rain-grown crop of Sudan American cotton is grown under much more primitive and difficult conditions than the irrigated crop of Sudan Sakel, and is of course of much lower value and quality, it is not surprising to find that the system of grading is not as strict. The crop in the various areas is grown under the supervision of the Department of Agriculture, which makes itself responsible for the purchase of the cotton, its grading, ginning and subsequent sale abroad The Government have established ginneries, equipped with batteries of saw gins, in different districts. The cultivators bring their sacks of seed cotton to the ginnery in their area, where they are weighed and purchased. There are no fixed standards established for grading, the levels in force in the various areas depend largely upon the views of the Inspector of Agriculture or other person in charge, and may change somewhat as the personnel changes. The question of standards is discussed in the last section of this paper. The regulations allow for four full grades of cotton, 1-4, but in many districts only three grades are in effective use The prices for the different grades are fixed by the Government according to prevailing economic conditions and to the requirements of current policy In general, however, Grade 1 cotton commands a marked premium over Grade 2 cotton, and Grade 2 over Grade 3 The result of this is that the hand sorting of seed cotton prior to sale is practised by the cultivators, in some areas on a large scale, in others only a little. Dirty and stained locks of seed cotton are removed to effect an increase in the grade of the bulk and so qualify for the higher price.

Each ginnery is allocated a mark, to which is added the appropriate grade number, for the purpose of bale identification. In the Nuba Mountain area of Kordofan the ginnery marks all include the letters NM. Some of the ginneries in this area are at present closed because of the curtailment of cotton growing, for reasons given in Section VI. For completeness, however, a full list is given of the various ginneries and their marks:—Talodi—NMT; Kadugli—NMK or NMKK, Lagowa—NMKL; Kalogi—NMKA, Abu Gebeiha—NMKC, Um Berembeita—NMKB; Dilling—NMKD Cotton from the recently developed flood irrigation area of Abu Habl, of the BAR SP. 84 type, is marked NMAH

In Equatoria the Meridi ginnery uses the mark MER Cotton grown in the Upper Nile province was ginned at Sennar under the mark UNM.

(ii) Irrigated Cotton

As mentioned above, the only appreciable crop of perennial irrigated American cotton now grown in the Sudan is that from Zeidab This cotton is grown, graded and marketed under the control of the Sudan Plantations Syndicate. It is classified under six full grades, ranging from N down to 6N. Half grades are not in general use except at the upper end of the scale, where the highest quality cotton is classed as Grade 1 extra, and marked XN The proportions of trash and stained cotton are the major factors considered in determining grade; staple length is also considered to a limited extent.

V. THE SUDAN SAKEL CROP

(*a*) CHARACTERISTICS AND PRODUCTION.

The main Gezira crop from the concessions of the Sudan Plantations Syndicate and the Kassala Cotton Company is now raised on an area exceeding 200,000 feddans. The quantity fluctuates according to growing conditions and pest and disease attack. In a good season it may amount to more than a million kantars,* or roughly 250,000 bales (400 lb.). In a

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* In the Sudan the statistics of production are expressed in terms of kantars of seed cotton, of weight approximately 312 lb One kantar of seed cotton is roughly equivalent to 95 lb. of ginned cotton in the case of Egyptian varieties, and about 90 lb. for American types Thus 4 kantars of seed cotton is roughly equivalent to one bale of 400 lb.

Table I
Sudan Cotton Crop : Production by Varieties
(in thousands of kantars 1 kantar = 100 lb of lint cotton, approximately).

	Average 1930/31 to 1939/40	1940/41	1941/42	1942/43	1943/44	1944/45	1945/46	1946/47	1947/48	1948/49 (Estimate)
SUDAN SAKEL										
Gezira S P S	582	682	686	809	530	819	539	Sakel 345	333	375
Gezira K C C	105	170	152	196	119	207	121	X 1730A 467	371	464
White Nile Government Schemes	8	46	44	55	32	63	37	37	52	67
White Nile Private Estates	22	45	32	38	30	41	36	51	50	60
Gash (Kassala)	55	44	63	106	70	82	41	50	73	90
Tokar	61	107	36	90	36	146	108	95	105	51
Total	833	1092	1013	1294	816	1359	883	1046	984	1107
SUDAN AMERICAN										
(i) Irrigated—										
Zeidab	22	19	15	15	16	17	10	9	14	18
Berber and Dongola	17	9	—	—	—	—	—	—	—	—
Private Estates	5	2	—	—	—	—	—	—	—	—
Total	44	31	15	15	16	17	10	9	14	18
(ii) Rain-grown—										
Kordofan	86	62	94	14	11	21	6	2	25	70
Equatoria	11	5	5	1	2	1	2	5	10	11
Upper Nile	4	*	2	*	*	—	—	—	—	—
Total	101	68	102	15	14	22	8	7	35	81

Table II
Sudan Cotton Crop : Area by Varieties

(in thousands of feddans. 1 feddan = 1·04 acre)

	Average 1930/31 to 1939/40	1940/41	1941/42	1942/43	1943/44	1944/45	1945/46	1946/47	1947/48	1948/4)
SUDAN SAKEL										
Gezira S P S	166	168	168	167	167	167	158	Sakel 109	114	105
Gezira K C C.	27	40	40	40	40	40	38	X 1730A 97	96	102
White Nile Government Schemes	2	11	13	15	15	16	13	13	16	16
White Nile Private Estates	7	12	12	12	11	13	14	15	16	16
Gash (Kassala)	28	22	32	31	32	31	27	27	33	47
Tokar	36	33	26	31	21	42	48	53	42	21
Total	266	285	289	295	286	309	298	314	314	307
SUDAN AMERICAN										
(i) Irrigated—										
Zeidab	5	6	5	5	5	5	5	3	5	5
Berber and Dongola	5	3	—	—	—	—	—	—	—	—
Private Estates	2	1	—	—	—	—	—	—	—	—
Total	12	9	5	5	5	5	5	3	5	5
(ii) Rain-grown—										
Kordofan	81	82	78	20	14	19	4	3	23	66
Equatoria	14	11	9	2	2	1	2	3	8	9
Upper Nile	5	4	5	5	*	—	—	—	—	—
Total	100	96	92	27	16	20	6	6	31	75

Notes on Tables I and II

(i) An asterisk denotes less than 500 kantars or feddans
(ii) The White Nile Government Schemes include Gondal, Abdel Magid, Fatisa, Hasaba, Um Gerr and Wad Nimr
(iii) White Nile Private Estates include Ed Dueim, Mahdi and others
(iv) The separate figures for yield and area have been rounded off to the nearest thousand, and consequently their sums may not agree exactly with the printed totals.

Table III
Results of Fibre and Spinning Tests, Gezira and Gash Cottons

	Effective length ($\frac{1}{32}$ inch)	Short fibre (%)	Mean fibre weight per cm (10^{-8} gm)	Immaturity count* (N–D) %	Maturity ratio	Standard fibre weight per cm (10^{-8} gm)	Trash content (%)	Lea count-strength products			Highest standard count
								80s	100s	120s	
(i) GEZIRA											
XGS	51	29	144	72–6	1·03	140	1·1	2540	2350	2160	107
GS	51	27	141	66–7	0·995	142	1·0	2630	2420	2210	115
XG2S	50	30	144	70–8	1·01	143	1·2	2610	2370	2160	108
G2S	49	30	141	69–7	1·01	140	1·3	2540	2330	2080	106
G3S	48	29	145	68–7	1·005	144	1·3	2580	2330	2100	107
G4S	46	32	148	68–7	1·005	147	1·5	2530	2230	2020	100
G5S	45	31	138	62–10	0·96	144	1·7	2440	2160	1920	94
G6S	45	30	138	60–9	0·955	145	2·4	2400	2140	1880	92
XGL	50	29	162	72–6	1·03	157	0·8	2370	2070	—	88
GL	50	28	156	67–7	1·00	156	0·8	2410	2050	—	89
XG2L	50	29	167	74–6	1·04	161	0·8	2410	2070	—	89
G2L	48	31	165	71–6	1·025	161	1·0	2340	2010	—	85
G3L	48	29	164	63–7	0·98	167	1·2	2230	1850	—	79
G4L	46	33	159	69–5	1·02	156	1·3	2130	1770	—	73
G5L	46	33	156	63–9	0·97	161	1·6	2070	1730	—	71
G6L	45	34	151	58–10	0·94	161	1·4	2040	1660	—	68
(ii) GASH											
KS	49	27	150	70–5	1·025	146	1·6	2680	2390	2120	111
K2S	49	29	141	65–7	0·99	142	1·9	2650	2360	2080	108
K3S	49	29	142	67–7	1·00	142	2·2	2680	2390	2140	111
K4S	48	29	137	57–11	0·93	147	2·1	2710	2430	2160	113
K5S	47	30	133	59–11	0·94	142	3·0	2690	2400	2110	110
K6S	45	34	113	48–15	0·865	131	5·5	2580	2280	2070	102
KL	50	32	157	68–6	1·01	155	1·4	2340	2020	—	85
K2L	49	30	158	64–7	0·985	161	1·7	2400	2060	—	89
K3L	47	30	156	62–8	0·978	161	1·9	2400	2030	—	88
K4L	48	32	143	58–12	0·93	154	2·4	2380	2080	—	89
K5L	46	32	154	60–9	0·955	161	2·2	2355	2000	—	85
K6L	44	38	127	50–16	0·87	146	4·6	2175	1800	—	76

* N = " normal " D = " dead "

poor season the yield may fall to about 600,000 kantars or 150,000 bales. Figures for the area under cotton and the total yield during recent years are given in Tables I and II.

The Abdel Magid area is the largest of the White Nile Alternative Livelihood Schemes and now grows more than 10,000 feddans of cotton, giving a crop of about 10,000 bales in an average season. The other areas in the Livelihood Scheme are much smaller and their yields and areas are included in the figures given in Tables I and II. The group of private estates irrigated by pumps drawing water from the White Nile grow about 11,000 feddans of cotton each year. The area owned by the Mahdi accounts for most of this.

The Tokar area varies from about 20,000 to 50,000 feddans, according to flood conditions, with an annual crop of 30,000 to 150,000 kantars, *i.e.* about 7,000 to 35,000 bales

The area under cotton in the Gash fluctuates less than in Tokar, because of greater control of the flood waters. The crop usually amounts to between 10,000 and 25,000 bales, it is generally smaller than the Tokar crop

Fibre and spinning tests are made annually at the Shirley Institute on a range of samples of the commercial Sudan Sakel crop. It is only within recent years that arrangements have been made to test a representative series of samples covering the more important grades and types. These samples are received from a number of sources, including the Raw Cotton Commission (previously the Cotton Control, Raw Cotton Section), the Sudan Plantations Syndicate, the Sudan Government and the Empire Cotton Growing Corporation. The results of tests obtained to date, whilst not sufficiently extensive to provide an accurate measure of the quality of a particular type in a given season, nevertheless enable a broad picture to be obtained of the character of the different grades from the various crops.

The samples examined in most detail are the Domains Sakel and X 1730A types of the main Gezira and Gash crops For ease of description in referring to these cottons, we shall use G(S) to denote Domains Sakel grown in the Gezira, a specific grade of it will be given its correct mark, XG2S, G3S, *etc.*, according to usual trade practice Similarly G(L) is used for the X 1730A type from the Gezira, K(S) for Domains Sakel from the Gash, and K(L) for X 1730A from the Gash.

Average values of fibre and spinning test results, made on representative samples of the 1944/45, 1945/46 and 1946/47 crops in different grades of these styles of cotton, are given in Table III

As previously outlined in this paper, grade is a composite classification based upon a number of widely different characteristics such as trash content, proportion of stained lint and, in some cases, staple length, feel, and lustre Consequently the grade classification for any one type cannot be expected to be exactly, or even closely related, to any single measured character of the fibre or the processed yarn We can only show the average tendency for fibre and yarn characteristics to vary with grade and type

The relation between grade and trash content will be considered first. The trash content has been measured by tests made on the Shirley Analyser, a machine designed to separate clean lint from impurities such as broken leaf, stalk and other forms of dirt. The average results for trash content, given in Table III, are plotted in the diagram of Fig 1 Reference to this diagram shows that, grade for grade, Gezira cotton of both the (S) and (L) types is cleaner than Gash cotton. There are two main causes of this

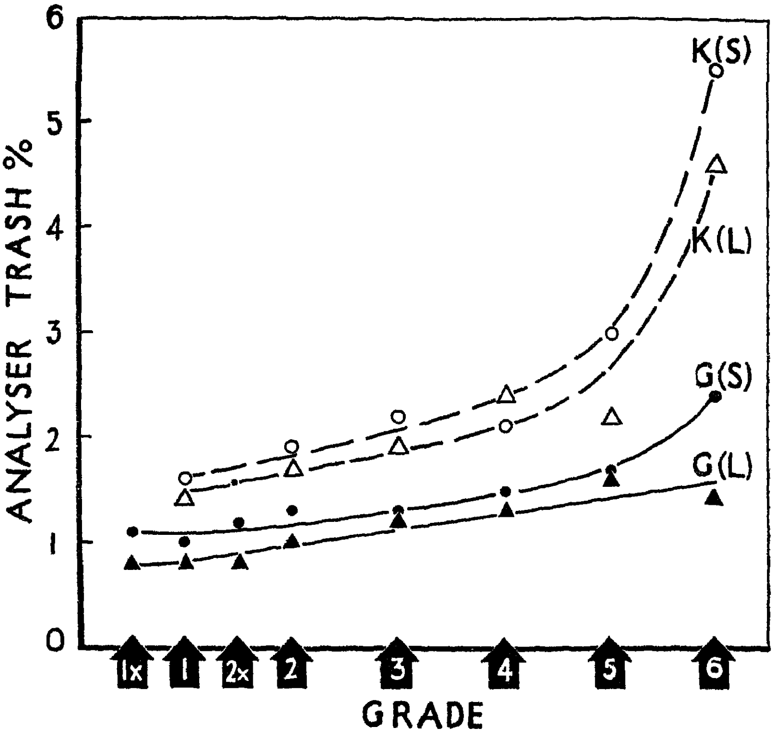

Fig 1

difference In the first place there is no close co-ordination of grading practices in the two areas. Cotton classed as Grade 2 in the Gezira would not necessarily be classed as Grade 2 in the Gash. Secondly, growth conditions in the two areas are very different and apparently plants grown in the Gezira do not shed as much bract and leaf material on to open bolls as plants grown in the Gash The more regular and frequent pickings made in the Gezira, arising from the steadier development of the crop, is also conducive to the gathering of clean lint Pickings are made less frequently in the Gash and consequently there is greater opportunity for the lint to become contaminated with shedding plant debris. In addition to the effect of environment on trash content there are differences due to variety G(L) cotton is consistently cleaner than G(S) cotton of the same numerical grade, and, at least in the better grades K(L) is cleaner than K(S) That this effect does not arise out of environmental differences is shown clearly by the results of tests on samples from controlled variety trials In 18 cases out of 20 recent pairs of comparisons, each pair grown under identical conditions, X 1730A was cleaner than Domains Sakel On the average Domains Sakel contained nearly 30 per cent. more trash than X 1730A

The variation of staple with grade is shown graphically in Fig 2 In this diagram the results for "Effective Length" are plotted according to type and grade. The effective lengths of the G(S) marks fall fairly regularly from a value of about 51/32 inch in Grade 1 Extra to 45/32 inch in Grade 6 The highest grade of K(S) cotton averages about 48/32 inch, somewhat shorter than the highest grade of G(S) cotton. The middle grades of K(S) cotton are, however, longer than the corresponding grades of G(S) cotton.

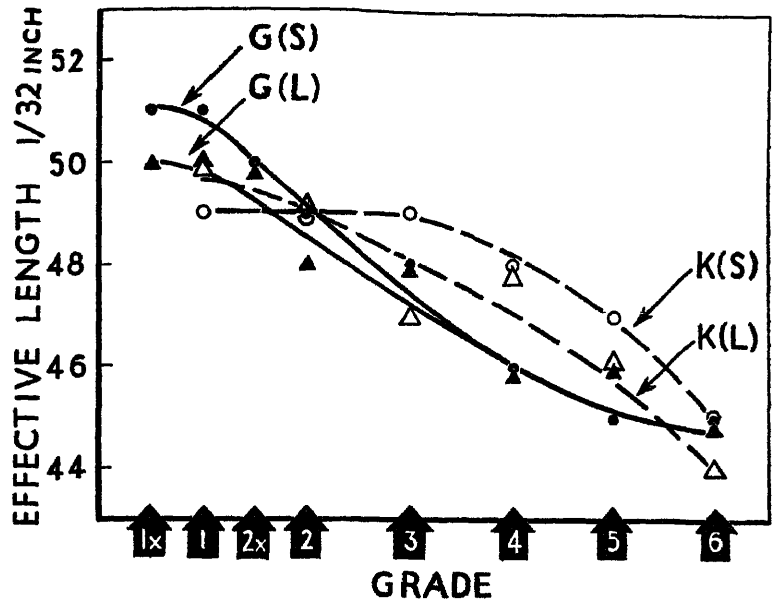

Fig 2

For the X1730A type of cotton the top grade of G(L) is slightly longer than the top grade of K(L), but the reverse applies over the bulk of the middle grades

The greater difference between the staple of the highest and lowest grades of Gezira cotton compared with Gash cotton may be expected in view of the differences between grading practices in the two areas In the Gezira direct attention is paid to staple length in allocating the appropriate grade classification to a given bulk of cotton Other things being equal, cotton of long staple is classed in a higher grade than cotton of shorter staple In the Gash, however, staple length is not directly considered in determining grade. Although the length of Gash cotton shows a tendency to fall with falling grade this does not occur as a result of the system of grade classification but because variation in staple length is loosely associated with variation in other factors which are noted and used in determining grade Cotton picked early in the season is generally graded high because it is clean, and free from stain associated with pest attack. Cotton from the end of the crop is usually dirtier, contains increased amounts of stained material, and is given a low grade These low grade cottons are often shorter than the earlier and higher grades, either because of the effects of pests or diseases on the plant or because of the decline in favourable growing conditions as the season progresses.

The results of "Immaturity Counts" show no consistent difference between the fibre immaturity of (S) and (L) cotton of the same grade and origin. In both the Gash and the Gezira, maturity falls with grade, partly arising from change in growth conditions and partly from the effects of pest and disease on the plant. Reference to the diagram in Fig. 3 indicates that the decline in maturity from top to bottom grade is more pronounced for Gash cottons than for Gezira cottons, not unexpected in view of the differences in irrigation and growth in the two areas.

The figures for "standard fibre weight per cm" in Table III show that Domains Sakel, with an average value of about 143 is appreciably

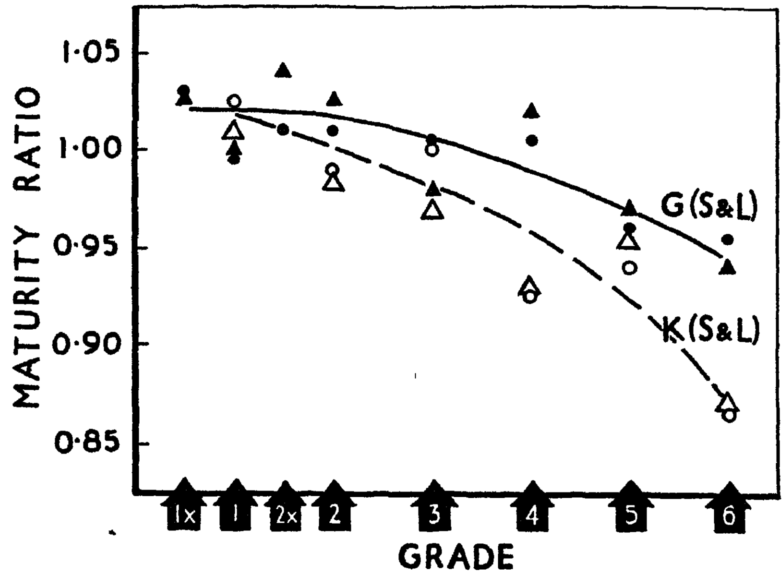

Fig. 3

finer than the X 1730A type with an average of about 160. In each case the same average figures for fineness have been given by Gezira and Gash material. Although there is no gross over-all "place" effect, the results of annual tests on experimental material show that environmental differences sometimes occur. In some seasons it has been found that all strains from one variety trial in one locality have given somewhat higher values than the same strains grown at a different place.

For both Domains Sakel and X 1730A cotton from the Gash, the standard fibre weight is less for Grade 6 than for the higher grades, presumably on account of the particular growth conditions in this area.

Routine spinning tests have been made in the Shirley Institute spinning rooms on a wide range of samples of Sudan Sakel. The spinning procedure is standardised for ease of comparison and rapidity of testing All samples of Sakel are combed, with 20 per cent. waste removed, and spun with a twist factor of 3·5 The average lea count-strength products of spinnings made on samples of different grades and types of the Gezira and Gash crops are given in Table III.

The figure given for "Highest Standard Count" of a cotton is not the highest count to which the cotton may be spun. For combed yarns it is taken to be the highest count which has a lea count-strength product greater than or equal to the arbitrarily chosen level of 2,250. The highest standard count should be regarded as providing a single figure, partly summarising the results of several spinnings in different counts, which may be used in making general comparisons of the yarn strength of different samples of cotton. For a fuller discussion of this measure see Parts I and II of this series and also a recent paper by C. Underwood in *Empire Cotton Growing Review*, 1949, Vol 26, p 1.

For the Domains Sakel grown in the Gash, reference to Table III indicates that the yarn strengths of the first five grades are little different, with the highest standard count averaging about 110. For Domains Sakel from the Gezira there is, however, a progressive decline in yarn strength from Grade 1 to Grade 6 Alternatively, we may make the comparison on the basis of

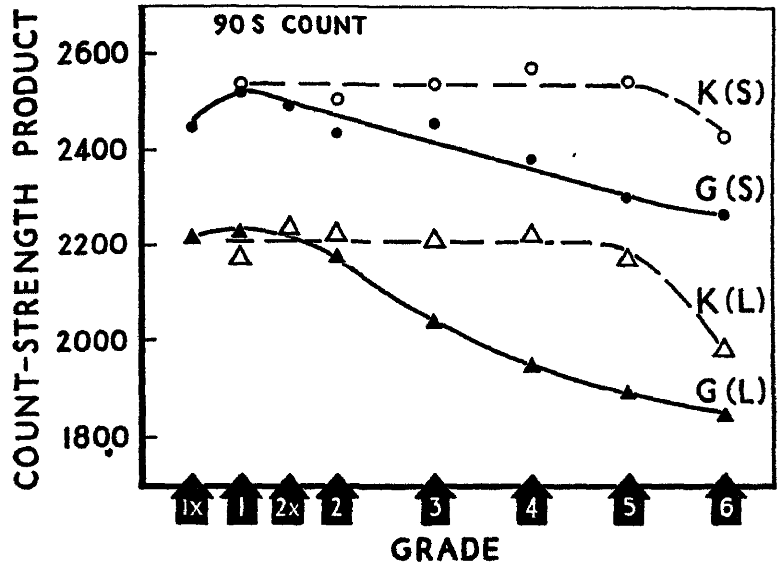

Fig. 4

count-strength product. For ease in comparison, and for increased accuracy, we use in this paper the average lea count-strength product of the 80s and 100s spinnings. (The procedure is justified because of the well-known linear relation between count-strength product and count for any cotton. Consequently the average of the 80s and 100s results gives an unbiased estimate of the count-strength product in 90s count, one subject to less experimental error of determination than either of the separate count-strength products.) The average count-strength product of 90s K(S) cotton in Grades 1-5 is about 2,490. For G(S) cotton the count-strength product falls from about 2,520 at Grade 1 to 2,300 at Grade 5. Grade K6S averages a product of 2,430 compared with 2,270 for G6S. It will be noted that the strength of XGS is somewhat lower than that of GS

The X 1730A or "L" type of cotton gives yarn strengths appreciably below those of the Domains Sakel. The top five grades of K(L) cotton average about 87 for highest standard count, falling to about 76 for K6L. This may be compared with a steady decline from a figure of 89 for the better grades of G(L) cotton down to 68 for G6L. On the basis of lea count-strength product of 90s yarn, the average of grades KL to K5L Gash cotton is about 2,210 falling to 1,990 for K6L. This compares with figures of 2,230 for the higher grades of G(L) cotton falling progressively to 1,850 for G6L.

In Fig. 4 the average count-strength product of 90s yarn has been plotted against the corresponding grade category for the Gezira and Gash types of both S and L cotton. The diagram enables a quick visual comparison to be made between the strengths of the two types in both areas and indicates how the strength varies through the different grades

A comparison of the characteristics of Sudan Sakel cotton with some of the long-staple types from Egypt is of practical interest. In the second paper of the present series (Part II, Egypt) a summary is given of the fibre characteristics and results of spinning tests on samples of various Egyptian cottons. The average values quoted below are obtained from samples which include some additional to those reported in the earlier paper

The most interesting comparisons are those between Egyptian Karnak and Sudan Domains Sakel, and between Egyptian Menoufi and the "L" (X 1730A) type of Sudan Sakel. In Table IIIA we give test values on samples of Karnak which have averaged about grade F.G. + ¼ (or Type 155B in the Raw Cotton Commission list), and also reproduce the test values for G3S from Table III.

Table IIIA

Type	Effective length (1/32″)	Short fibre %	Standard fibre weight per cm (10^{-8}gm.)	Trash content %	Lea count-strength product		Price, pence per lb. (List issued May 9th, 1949).
					80s	120s	
Gezira Sakel G3S	48	29	144	1·3	2580	2100	42·05
Karnak 155B F.G. + ¼	49	32	136	1·7	2640	2150	42·05

These two cottons are listed at the same price but differ slightly in their characteristics. Karnak in grade F.G. + ¼ is slightly longer and finer than G3S and gives a slightly stronger yarn. The small advantage of increased yarn strength is counterbalanced by a small excess of trash, Karnak containing 1·7 per cent. compared with 1·3 per cent for G3S.

It might be added that the increase in yarn strength of Karnak Type 155B over G3S is rather less than would be expected from the values of its length and fineness The explanation of this appears to lie in the fibre strength. Bundles of fibres broken on the Pressley Tester* have given figures for intrinsic fibre strength which are lower for Karnak than for Gezira Sakel. This lower fibre strength of Karnak partly counterbalances the advantages of the greater staple length and fineness.

A number of spinners have remarked that Karnak tends to give a somewhat more neppy yarn than Gezira Sakel. Although a sample of average-grade Karnak is longer, slightly more irregular in staple, slightly finer and possibly a little more immature than a sample of medium-grade Gezira Sakel we hesitate to ascribe the complaint of greater proneness to neppiness to any one of these small differences Experience at the Shirley Institute has shown that increased staple length and fineness, fibre irregularity and fibre immaturity all tend to give increased neppiness. It is possible that the cases in which complaint is made of greater neppiness of Karnak have arisen because of the unavoidable combination of all these small differences, but no conclusive evidence is available on this point

The Egyptian Menoufi† cotton averages 47/32 inch in effective length and about 153 in standard fibre weight per cm It is, therefore, of about the same length but somewhat finer than the middle grades of Gezira G(L) type of cotton The results of spinning tests on a range of samples indicate that Menoufi gives yarns which are a little stronger than those spun from

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*For a description of the details of the Pressley Fibre Strength Tester see *ASTM Bulletin*, October, 1942, pages 13-17 It is not the purpose of the present paper to give an exhaustive investigation into the relation between fibre characters and yarn strength It is hoped to publish a separate paper on this aspect of the work at a future date, and incorporate in it the relations found to exist in a general range of world cottons and not Sudan Sakel in particular

†This comparison refers to the original issue of Menoufi seed, the recent introduction of Improved Menoufi is finer and of greater intrinsic fibre and yarn strength than "ordinary" Menoufi

the middle grades of Gezira G(L) cotton and a little weaker than those from the middle grades of Gash K(L) cotton. The results on a limited number of tests made on the Shirley Analyser show that Menoufi cotton contains a little more trash than the middle grades of K(L), and appreciably more than the middle grades of G(L) cotton.

Test results on samples of Sudan Sakel from other areas in the country are not available in the same detail as for the main Gezira and the Gash crops Where samples have been received in some or all seasons from 1942/43 to 1946/47, the average values of tests made on the material are given in Table IV (p 70).

A number of samples of the top grade, T1C, of the Tokar crop grown from the X 1730A seed have been received and tested at the Shirley Institute. Comparison between the fibre characters and the yarn strength of this type with the value for G(L) cotton indicates that it is more or less equivalent to about XG3L or G2L. The T1C samples have, however, give a value of 1 9 per cent for the trash extracted by the Shirley Analyser, compared with about 1 0 per cent for typical G2L cotton. Consequently the cash value of T1C would be considered lower than that of XG3L or G2L on account of this excess trash. So far, insufficient tests have been made on the other three grades of this crop to permit the drawing of any broad conclusions.

The Mahdi Pump Scheme area on the White Nile now grows Domains Sakel cotton, although a few seasons ago some X 1730A type was also produced The results of tests on samples of the former type (see Table IV) show that the higher and middle grades of Mahdi Domains Sakel are shorter and of lower yarn strength than the corresponding grades of the main-crop G(S) cotton. The lowest grades of the Mahdi cotton are shorter than the better grades, and about equal in length and of slightly stronger yarn strength than the bottom grades of G(S) cotton Although a full series of trash measurements have not been carried out on this set of samples, the results available show that, in the middle and bottom grades, the Domains Sakel from the Mahdi area is dirtier than main-crop Domains Sakel from the Sudan Plantations Syndicate zone. Consequently there may be a marked difference in character between two samples of the same grade number, one from the Mahdi area and the other main-crop Gezira Domains Sakel. This result is not surprising in view of the cottons being grown in different areas, assessed for grade by different sets of seed cotton classifiers who do not necessarily work to the same standards, and finally being ginned in different ginning centres It should be added that these results are based mainly on samples of Mahdi cotton from the 1944/45 crop, and a wider range of material might show slightly different tendencies

In the 1943/44 and 1944/45 seasons, when the Mahdi area also grew some of the L type of cotton, a few tests were made on some of the higher grades, from MXL to MX2L These samples averaged about 48/32 inch in effective length, 164 in standard fibre weight per cm. and 85 in highest standard count determined from spinning tests. These figures do not differ greatly from those given by corresponding grades of main-crop G(L) cotton, the Mahdi samples being a little shorter in staple and slightly weaker in yarn strength.

A number of tests have been made on commercial samples of cotton from the Abdel Magid area, in which the X 1730A strain cotton is grown The results of these tests are given in Table IV and may be compared with results for G(L) cotton given in Table III Grade for grade, the Abdel Magid cotton is longer than the main-crop G(L) cotton and also of higher

Table IV

	Effective length ($\frac{1}{32}$ inch)	Short fibre (%)	Mean fibre weight per cm (10^{-8} gm.)	Im-maturity count (N–D) %	Maturity ratio	Standard fibre weight per cm (10^{-8} gm.)	Trash content (%)	Lea count-strength products			Highest standard count
								80s	100s	120s	
Tokar:											
T1C ...	48	26	157	65–8	985	159	1·9	2300	2000	—	83
Mahdi											
MXS to MX2S	49	30	149	67–6	1·005	148	1·2	2540	2300	2090	105
M2S to M3S	47	30	135	56–11	0·925	146	2·3	2550	2280	2090	104
M4S to M5S	45	30	125	49–14	0·875	143	6·3	2530	2350	2140	109
MXL to MX2L ..	48	30	162	62–8	0·97	167	—	2300	2030	—	84
Abdel Magid											
ALX1 to ALX2	51	28	161	75–2	1·035	156	0·9	2525	2190	—	96
AL2 to AL3	50	32	164	69–5	1·02	161	1·0	2365	2020	—	87
AL4 to AL5	48	33	161	68–7	1·005	160	1·3	2265	2915	—	81
AMX1 to AMX2 .	52	26	136	53–7	0·93	146	—	2810	2420	2230	118
White Nile											
WNX1 to WNX2	51	29	142	71–5	1·03	138	1·2	2660	2370	2140	110
WN2 to WN3	50	30	145	70–6	1·02	142	1·4	2640	2320	2080	106
WN4 to WN5	49	33	139	64–6	0·99	140	1·7	2560	2260	2000	101
Gondal.											
GNDL1 . ..	48	31	159	63–7	0·98	162	1·4	2310	2010	—	84
GNDL2 .	48	32	159	61–7	0·97	164	1·7	2260	1890	—	81
GNDL3 to GNDL4	45	35	148	57–11	0·93	159	2·8	2130	1730	—	74

yarn strength. The figures for trash content, measured by the Shirley Analyser, show that Abdel Magid cotton contains about the same amount of trash as G(L) cotton of the same grade, as would be expected because the Abdel Magid crop is graded and ginned at the ginnery which serves the northern part of the Sudan Plantations Syndicate and the Kassala Cotton Company area

Analyser tests made on samples of Domains Sakel cotton from the White Nile Alternative Livelihood areas have given slightly greater trash figures than tests on samples of corresponding grade of main-crop Sakel of the G(S) type The higher grades of White Nile Sakel are of about the same staple as the higher grades of G(S) cotton, but in the lower grades the staple does not fall off as rapidly as the G(S) cotton. This may be explicable on the grounds that the two crops are graded and ginned at different centres, in addition to differences in growing conditions in the two areas. The yarn strengths of the best grades of White Nile cotton are not quite so high as the best grades of G(S) cotton, but there is little consistent difference in strength between corresponding samples of middle and low grade.

The results of tests on a limited range of samples of X 1730A grown on the Gondal area on the White Nile are given in Table IV. These few results indicate that grade for grade this part of the Gondal crop is of somewhat shorter staple length and lower yarn strength than the corresponding main-crop G(L) type of cotton.

Since writing this paper the results of tests on the 1947/48 crop have become available Compared with the average figures in Table III, the top grades of main-crop G(S) cotton were a little longer in staple and gave slightly better yarn strengths G(L) cotton was of similar staple but slightly more irregular and contained more trash, giving slightly lower strengths than average. The Gash K(S) and K(L) types also gave more trash than usual Compared with corresponding results in Table IV, the Abdel Magid grades contained more trash, the top grades of Gondal were slightly shorter and weaker, and White Nile cotton was very similar.

(*b*) SEED MAINTENANCE AND MULTIPLICATION.

Since the Domains Sakel and X 1730A strains have now both been grown virtually unchanged in character (apart from seasonal fluctuations and variations associated with area of growth and with classified grade) for a period of many years, the Sudan Sakel crop has gradually established a firm market among spinners of Egyptian-type cotton in both this country and abroad The present policy of the Sudan is to maintain the growth of these types in quantities rather greater than in the immediate pre-war seasons. Nevertheless intensive breeding is in progress on both types and has two main objects

The first general aim of the Sudan Government and the Sudan Plantations Syndicate is to maintain the *average* qualities of each type at about the present levels since the cottons are giving satisfaction to the consumer. Part of the breeding work of the Research Division is devoted towards improving the uniformity of the two crops, both with respect to the character of the raw cotton and of the plant, and this work links up with the practical problem of propagation of uniform seed stocks to avoid all risks of degeneration. A broad outline of the methods of seed propagation and the development of purified seed stocks is described in this section of the paper. The second aim of the authorities is to breed new stocks of seed having fibre characters identical with those of the present types but with improved plant character such as increased resistance to pest and disease attack, earlier habit, *etc.* This part of the work is described in Section VII of the paper.

As mentioned previously, the early seed production policy in the Sudan depended upon obtaining fresh stocks of high quality Domains Sakel seed from Egypt, seed which had been grown under controlled conditions on the farms of the Egyptian State Domains The seed from Egypt was multiplied on the Barakat Seed Farm of the Sudan Plantations Syndicate and issued for cultivation in the Gezira Fresh supplies of Domains Sakel seed were imported at irregular intervals, the last major importation being in 1935 This policy became impossible following the decline and ultimate extinction of Sakel cotton in Egypt. A small entry of seed in 1941 was subjected to trial, found to be of inferior quality, and was not used for multiplication purposes.

A new seed multiplication programme for Domains Sakel cotton has become gradually established since the middle 1930's The Barakat seed farm now maintains a nucleus stock of seed which is regularly "rogued" for removal of off-type plants. Surplus seed from this nucleus area is expanded in the following season and the crop gives sufficient seed for growth on the main propagation area on the farm in the third season Seed from this crop is used in the next season to plant about half of the Gash area. The Gash acts as a filter for blackarm disease, the seed grown there is much freer from infection and is returned in the following year for planting of about half of the much larger Gezira area

A similar system is used for the X 1730A strain, multiplication from nucleus stocks is carried out on the Hamid el Nil Seed Farm under isolated conditions, planting is done for one year in the second half of the Gash and the seed is then returned for planting the remaining Gezira area not under Domains Sakel. The nucleus for X 1730A was not, of course, derived from Egypt but from the leaf-curl resistant selection made in the Sudan as described in Section II(*b*)

A few years ago the Government and Syndicate decided that the seed supply of the Domains Sakel strain should be purified to obtain a more uniform nucleus stock containing plants all of typical Sakel type and bearing lint of typical Sakel quality. A nucleus field of Domains Sakel on the Barakat Seed Farm, sown with hand-picked seed and rogued three times by the Inspector in charge of the Farm, was carefully examined. From the field 268 typical trees were chosen and various characters were analysed by S. H. Evelyn at the Gezira Research Farm. Of these selections, 14 were immediately discarded on account of the poor appearance of combed halos and the remaining 254 plants were examined for seed weight, lint weight, ginning out-turn and mean maximum fibre length on stretched seed cotton fibres The mean values of these characters were determined and it was found that there were marked differences between plants A "purity" test was applied and only 43 plants were retained, each of which gave values for the four characters falling within fairly narrow limits of the corresponding mean values given by all plants in the bulk

In the 1943/44 season separate progeny rows of the 43 purity selections were grown and the material from them was again examined Selfed seed of 13 of the purest families was bulked together for multiplication In the 1944/45 season a small bulk quantity of Evelyn's Selected Sakel was grown at the Barakat Seed Farm and a sample of the lint was sent to the Shirley

Table V
Comparison of Selected and Standard Domains Sakel

	Effective length ($\frac{1}{32}$ inch)	Short fibre (%)	Mean fibre weight per cm (10^{-8} gm)	Immaturity count (N–D) %	Maturity ratio	Standard fibre weight per cm. (10^{-8} gm)	Trash content (%)	Lea count-strength products			Highest standard count
								80s	100s	120s	
1944/45 —											
Selected ..	50	26	150	66–6	1·00	150	1·2	2640	2380	2110	109
Standard	49	31	149	65–8	0·985	151	1·3	2580	2350	2040	105
1945/46 —											
Grades 1-3 Selected	49·7	29	139	70–5	1·025	136	1·3	2580	2340	2085	108
Standard	49·3	30	143	67–6	1·005	142	1·3	2265	2180	2060	83
Grades 4-6 Selected .	47·3	34	134	63–9	0·97	138	1·6	2520	2210	1950	99
Standard	47·0	32	135	62–10	0·96	141	1·3	2520	2240	2020	100
1946/47 — Gezira											
Grades 1-2 Selected	50·7	33	140	72–5	1·035	135	1·2	2700	2420	2165	113
Standard	51·0	29	143	74–4	1·05	136	1·2	2750	2390	2155	111
Grades 3-4 Selected	48·0	34	139	65–7	0·99	140	1·9	2565	2250	1975	101
Standard...	48·8	34	142	66–6	1·00	142	1·8	2640	2320	2030	105
Grades 5-6 Selected	46·8	33	137	59–9	0·95	144	2·1	2475	2150	1935	95
Standard	46·2	34	137	59–9	0·95	144	2·2	2460	2115	1875	92
1946/47 — Gash											
Selected .	46·8	27	134	58–11	0·935	143	2·5	2635	2310	2035	105
Standard	46·8	29	136	59–10	0·945	144	2·8	2640	2410	2095	110

Institute. This sample was compared with a sample of standard Domains Sakel grown on the Gezira Research Farm as it was not found possible to obtain a strictly comparable lot from Barakat. The results of these tests are given in Table V and indicate that the Selected Sakel was about $\frac{1}{32}$ inch longer in staple than Standard Sakel and not appreciably different in yarn strength.

In the 1945/46 season a number of wholly comparable pairs of samples were sent to the Institute for examination. Four pairs of Selected and Standard samples were grown on the Barakat Seed Farm and were classed by the Chief Cotton Classifier of the Sudan Plantations Syndicate in grades 1-4. Two other pairs of samples were from Variety Trials, one on the Gezira Research Farm and the other from Abu Wafi, near Turabi, in the northern part of the Gezira. These samples were classed as Grade 6. The samples have been divided into two groups, the first containing Grades 1-3 and the second Grades 4-6. The average test results on these groups are given in Table V. In the first group of samples the Selected Sakel was about $\frac{1}{64}$ inch longer than the Standard type and also a little finer as judged by standard fibre weight per centimetre. Spinning tests gave yarn strengths which were greater for the Selected than for the Standard. For some reason unexplained, the results given by the Standard Sakel in Grades 1-3 are anomalous for this type of cotton. Particularly in the coarsest count (80s), an exceptionally low yarn strength was obtained. This results in the 80s spinnings presenting a more favourable picture of the Selected type than the results in 120s spinnings, one which is not typical of the general behaviour. There was little difference in fibre length, fibre fineness or yarn strength in the second group of lower-grade cottons.

In the 1946/47 season 11 pairs of samples from different parts of the Gezira were sent by the Research Division to the Shirley Institute for examination. These varied from Grade 1 to Grade 6 and have been classified in three groups, each containing either three or four samples. Table V shows that possibly in Grades 3 and 4 the Standard type gave rather better results than the Selected, in Grades 1 and 2 there was little difference, and in Grades 5 and 6 the comparison was possibly in favour of the Selected type. The differences are small and cannot be regarded as significant.

In this season a set of five comparisons was also made at the Institute on material grown in the Gash under bulk cultivation conditions. The differences between corresponding samples of Evelyn's Selected Sakel and the Standard Main-crop Sakel was small, the latter type this time being generally slightly stronger. It might be added that since the material was grown under bulk conditions on different areas in the Gash, the comparison between the two types was not so rigid as in previous cases when the cottons had been grown together under almost identical conditions.

In all three seasons there have been no consistent differences between the appearance of the yarns in corresponding pairs of the two types, sometimes the Selected material being better and at other times the comparison going in favour of the Standard type. The results of tests to date indicate that there is no pronounced difference in the character of the cotton from the two seed stocks.

Side by side with these technical tests the usual wide range of field tests have been made in the Sudan. The results so far indicate that, although there is no large difference in gross yield between the Selected and Standard seed supplies, any difference which does exist is in favour of the more uniform Selected material. In particular, the Selected Sakel gives a higher proportion of its crop in the upper grades

The above programme has been described in detail to indicate the careful checks which are being made in the Sudan to ensure that there is not likely to be either any slow decline in quality, or a sudden change, in the characteristics of the Domains Sakel crop. If, after further trials, a decision is made to use the purified selected stock as the future nucleus of the crop, spinners will continue to receive the same quality of cotton as they have had previously for a period of many years.

VI. THE SUDAN-AMERICAN CROP

(*a*) RAIN-GROWN COTTON

The Nuba Mountains, the main area in the country for the rain-grown crop of American cotton, contain close on ten million acres of arable land of which only about six per cent. is under cultivation In the five seasons preceding the war the area under cotton was a little over 100,000 acres, or about one-sixth of the total cultivated The average crop during this period amounted to about 100,000 kantars (each of 315 rotls of seed cotton) or about 25,000 bales (400 lb.), and indicates the great progress which had been made from 1924 when cotton was first introduced as a cash crop and yielded less than 40 bales During the war it became necessary to restrict cotton growing, partly because of war-time difficulties of transport and marketing and partly because of the need for increased grain production. As a result, the area under cotton fell until it reached the low level of 4,400 acres in the 1945/46 season. The Government avoided the complete disappearance of cotton growing by keeping two ginneries open, so preventing the commercial seed stocks from becoming extinct During the later war years, and at the beginning of the post-war period, the price of grain rapidly rose and cultivators required little persuasion to grow it in preference to cotton Cotton prices have now been increased however and the peasants are anxious to grow cotton again as a cash crop The cotton area in the 1947/48 season showed an increase over the level in the previous season. In the 1948/49 season the area under cotton greatly expanded and the crop was trebled, reaching a level comparable with many pre-war years. Given favourable conditions and prices it may be anticipated that there are good prospects of large crops in this region.

Before the war, seed expansion from nucleus stocks was made at the Kadugli Sub-station and Farm of the Research Division, and in isolated areas where members of the staff could exercise a certain amount of supervision. The inauguration of the Abu Habl Scheme may prove a valuable help for bulking up seed stocks in the future The yields should be greater and more constant than in areas relying solely upon rainfall and so should materially increase the initial propagation rate An appreciable crop of BAR.SP 84 was grown on this scheme during the 1946/47 season in order to increase the seed stocks

Before the war the Upper Nile Province produced small amounts of rain-grown American cotton. The size of the crop showed marked seasonal fluctuations and rarely exceeded 1,000 bales As mentioned above, cotton growing ceased in this area during the war and there appear to be no immediate prospects of its commencing again on an appreciable scale

In Equatoria the peak production of rain-grown American cotton was in the 1935/36 season when it amounted to more than 5,500 bales. In most seasons it was considerably lower, usually about 2,000-3,000 bales During the later war years difficulties of transport caused the Government to cease giving active encouragement to cotton growing in this area and the crop fell to a low figure of about 200 bales in 1942/43, later increasing somewhat. The main areas are centred around Meridi and Yambio It is doubtful whether there are any prospects of large crops for export in the near future

Over a period of more than 20 years large numbers of cotton and spinning tests have been made on various samples of the different strains from experimental trials, and from propagation areas, in the Nuba Mountains The results of some of these tests are summarised in Table VI. For cottons under consideration at the present time, the results given in this table refer to samples received from the 1940/41 season onwards For some varieties of which growth has now ceased, the Table contains results from about 1936/37 onwards in order to include sufficient within one group to ensure that the average figures are reasonably reliable It may be added that Table VI contains many strains which have never emerged from the experimental into the commercial stage. Since this paper is written for reference of cotton breeders as well as industrial consumers it is felt that the inclusion of purely experimental material is desirable on the grounds that agricultural workers frequently interchange material and hence are often interested in the quality of strains of cotton tried elsewhere.

Pump Scheme Strain

Although the "Pump Scheme Strain" was developed for growth on the northern pump irrigation areas on the Nile (for its origin see Section II (*c*)) the rapid development of the Nuba Mountain area from the middle 1920's onwards resulted in far more of this cotton being produced under rain-grown conditions than under irrigation Table VI contains the results of tests on a range of samples of this cotton received over several seasons from the area around Kadulgi and Talodi. The effective length of the cotton has averaged 37/32 inch and its fineness as measured by standard fibre weight per cm is 192 Spinning tests* on samples of Pump Scheme Strain have given lea count-strength products of rather more than 2,200 in 40s count and about 2,040 in 50s count Since many of these samples have been grown under the best conditions of cultivation it is not surprising that samples of the commercial crop have averaged a yarn strength about seven per cent lower than the above figures

Included in the Table are average test figures obtained from two ranges of typical American cottons imported into this country from the U.S.A The first group of these American cottons have averaged about 36/32 inch (corresponding to approximately 1 inch staple length on the basis of the Official American Standards) and the second group about 40/32 inch (or about 1⅛ inch staple) It will be noted that, in common with most other Empire types of American cotton, Pump Scheme Strain is appreciably finer, more immature, and of higher yarn strength than U.S.A cotton of similar staple length.

BAR. SP. 84 (or BAR. 7/1)

Seed of the SP 84 variety was imported from Uganda in 1940 and in trials at Shambat was found to be partly resistant to blackarm disease The

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* Spinning tests on samples of all Sudan-American types have been made in carded qualities with a twist factor of 3 75

Table VI
Characteristics of Sudan-American types

Type	Effective length ($\frac{1}{32}$ inch)	Short fibre (%)	Mean fibre weight per cm (10^{-8}gm)	Immaturity count (N-D) %	Maturity ratio	Standard fibre weight per cm (10^{-8}gm)	Lea count-strength products				Highest standard count
							32s	40s	50s	64s	
Rain-grown											
Pump Scheme Strain	37 0	28	154	43–22	0·805	192	—	2220	2040	—	52
BAR SP. 84 .	37 9	34	151	38–25	765	197	—	2110	1890	—	45
NT 205/41 .	36 0	37	156	37–25	76	205	2060	1900	1700	—	35
/42 .	37 0	36	155	29–30	695	223	1790	1670	1430	—	23
/43	35 8	36	151	39–23	·78	194	2110	1920	1690	—	37
NT 58 /39 .	39 3	33	138	29–32	685	199	—	2280	2140	—	60
/42	37 2	38	155	34–28	73	213	—	2070	1840	—	43
NT 96 /40	37 2	36	143	31–31	70	204	—	2130	1980	—	49
XA 129	34 1	26	153	43–24	795	190	—	2270	2065	—	53
511 D	36 6	32	160	40–25	775	207	—	2060	1890	—	44
Deltapine	37 4	36	158	35–27	74	213	1830	1680	—	—	21
U S A Crop (i)	36 0	26	206	54–15	90	233	1910	1740	1530	—	28
U S A Crop (ii) ..	40 0	28	180	48–15	865	209	—	2120	1970	—	48
Irrigated											
Wilds (Zeidab)	46 5	32	161	53–13	90	179	—	2390	2250	2070	69
513	37 5	37	159	52–11	905	176	—	2150	1970	—	48
514 Sub-strains	41 5	28	166	59–8	955	174	—	2520	2330	2065	68
XA 1129	41 2	28	166	46–10	88	189	—	2550	2400	2120	69

strain BAR.SP 84 is the component carrying the B_2* resistance factor and was "sifted" out of the original bulk stock. Compared with Pump Scheme Strain, BAR.SP.84 is a fairly hairy type of plant, sufficiently hairy to withstand most jassid attacks in the Nuba Mountains and has a five per cent. greater ginning out-turn. BAR SP.84 also possesses the advantage of being appreciably earlier in growth than Pump Scheme Strain. Even with fairly early plantings BAR.SP.84 gives higher yields than Pump Scheme Strain, but under late conditions the difference is more marked. Because of the rapid spread of "harig" cultivation and the necessity for an early type, the immediate choice of a suitable commercial cotton for the Nuba Mountains now appears to lie between BAR.SP.84 and the NT 205/43 strain

The results of fibre and spinning tests on samples of BAR.SP.84 are given in Table VI. This cotton is about $\frac{1}{32}$ inch greater in effective length and is slightly coarser in standard fibre weight per cm. than Pump Scheme Strain, giving slightly weaker yarns. Selection, breeding and expansion of BAR SP.84 is still in progress in the Nuba Mountains and it may be added that the results of the latest tests available for this cotton gave little difference between its yarn strength and that of Pump Scheme Strain.

Over a period of years, it has been observed that yarns spun from Pump Scheme Strain are generally of better appearance with less neppiness than those spun from other strains of Sudan American cotton. Although Pump Scheme Strain is on the average more mature than the other strains from Kordofan listed in Table VI, the superiority is not always well marked and therefore does not appear to explain entirely the better yarn appearance associated with this cotton. It will be noted from the figures for percentage short fibre that Pump Scheme Strain is, on the average, more regular in staple than the other types. This greater fibre regularity would be expected to lead to better drafting in processing and so give improved yarn appearance

The slightly lower yarn strength and inferior yarn appearance of BAR.SP 84 in comparison with Pump Scheme Strain can only be detected when the averages of a number of tests on each cotton are taken into consideration. From a commercial point of view there is not a great deal of difference between the characteristics of the two cottons In any case from a general economic view, the differences which exist in favour of Pump Scheme Strain are outweighed by the superior agricultural advantages of BAR.SP.84. BAR.SP.84 did not arise as a single plant selection but has been developed from a number of plants sifted out of the heterogeneous Uganda S P.84 stock, There is a fair amount of genetic variance in the present seed stocks of BAR SP 84 and consequently further plant breeding might possibly be directed towards selecting a sub-strain more mature, and more regular in staple than the present type and so make the cotton an even more suitable replacement for Pump Scheme Strain.

BAR.SP 84 has been adopted in the newer cotton areas around Yambio in Equatoria and generally throughout the cotton growing regions in this province The former main type, 511D, is a little shorter, and of slightly coarser standard fibre weight than BAR.SP.84 and consequently gave somewhat lower yarn strengths.

NT.205 Strains

The strain NT.205/41 is derived from bulk progenies from selections made by the Research Division in 1940 from the Uganda variety SP 20, which itself was selected from the South African U4/4/2 variety NT 205/41 possesses many advantages needed for commercial success in the Nuba Mountains. It is a much earlier cotton than Pump Scheme Strain and has a ginning out-turn about 4½ per cent higher than this latter cotton Moreover it is resistant to jassid attack, has given greater yields than Pump Scheme Strain in a range of variety trials, and is heterogeneous for resistance to blackarm disease, one component of it carrying the B_2 factor Reference to Table VI indicates that NT.205/41 has a slightly shorter length, a little coarser standard fibre weight, and a lower yarn strength than Pump Scheme Strain The cotton is more immature and more irregular in staple than Pump Scheme Strain and gives yarns of inferior appearance

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* For a description of the various factors for blackarm disease, see Section VII (*a*)

NT 205/42 is a re-selection of NT.205/41 material, primarily sifted for greater ginning out-turn and yield The figures in Table VI show that the effect of the selection has been to increase the standard fibre weight per cm. and effect a marked decrease in yarn strength. This strain has been discontinued on grounds of unsatisfactory quality.

NT.205/43 is derived from several plants carrying the B_2 blackarm resistance factor segregated from the heterogeneous NT.205/41 stock This variety has all the desirable plant habits of NT.205/41 together with the increased resistance to blackarm disease. From an agricultural point of view there is little to choose between NT 205/43 and BAR SP.84. Tests on a range of the two cottons show that NT.205/43 is shorter in staple, possibly slightly more irregular, and of noticeably lower yarn strength than BAR.SP.84.

NT.205/45 is a recent selection of NT 205 material which has given good results in the field. So far only two samples have been tested at the Institute for fibre and spinning characters. The results of these two tests suggest that NT 205/45 is a little longer and stronger than NT.205/43 but possibly not quite so good as BAR.SP 84

NT.58 Strains

NT.58/39 originated from a selection made from an outcross in the 513 strain (suspected to be Webber × 513) and was chosen for earliness and lint quality. It is a large-bolled vigorous plant, fairly resistant to jassid and heterogeneous for blackarm resistance Fibre tests show that the cotton is longer and slightly coarser than Pump Scheme Strain and consistently more immature It has a greater yarn strength than Pump Scheme Strain. NT.58/39 gives markedly lower yields than BAR.SP.84 and consequently is not acceptable for growth in the Nuba Mountains

N.T 58/42 was selected by the cotton breeders from NT 58/39 and results of tests on samples sent to the Shirley Institute show that it is shorter in staple, and of coarser standard fibre weight. Because of this it has given yarns of appreciably lower strength than the parent stock. The cotton is unlikely to be adopted for general growth in the Nuba Mountains

N.T.96/40

NT 96/40 is a selection made from an importation from Nyasaland of hybrid material (from 57 × Over the Top). It was selected for quality and yield, and in a series of trials has given greater yield per acre than Pump Scheme Strain. NT.96/40 is a large-bolled plant, resistant to jassid and heterogeneous as regards resistance to blackarm disease It is of about the same length as Pump Scheme Strain but a little coarser in standard fibre weight and more irregular in staple Spinning tests indicate that its yarn strength is somewhat below that of Pump Scheme Strain

BAR NT 96 is the blackarm resistant component separated from NT 96/40 At the time of writing the only samples tested at the Institute are those grown under irrigation on a pump scheme where the seed was being increased As would be expected, the lint from this irrigated cotton is longer than the rain-grown NT 96/40 cotton; the yarn strength also showed an increase by an amount expected from the increase in fibre length. Further trials in rain-grown areas will, of course, be necessary to evaluate the importance of this strain relative to Pump Scheme Strain and BAR.SP.84.

Deltapine

Bulk supplies of the Deltapine variety (derived from a cross between the Foster and Express strains) were obtained from the Delta and Pinelands Seed Co , U.S A. For a number of years this cotton was grown experimentally in comparison with other types in Kordofan A small crop was raised by native cultivators and appeared on the market a few seasons ago Deltapine cotton is of fairly early habit, has a high seed weight and ginning out-turn and gives yields above those of Pump Scheme Strain The cotton does not contain any major factors for blackarm resistance, but is not entirely susceptible to the disease because of an accumulation of a number of minor genes Steps were being taken at Shambat to improve the resistance by crossing the cotton with the NT 61/38 strain (which contains the B_2 factor) and subsequently back-crossing, but the decision to abandon the cotton from the commercial programme made this work unnecessary

The decision of the Department of Agriculture to withdraw the strain from commercial cultivation was made on the basis of its fibre characteristics and not on its agricultural performance. The average results from a series of tests made on samples of this cotton are contained in Table VI. Deltapine cotton is of about the same staple length as the Pump Scheme Strain, contains more short fibre, is of greater standard fibre weight per cm and gives yarns of markedly lower strength. The lea count-strength product in 40s count averages about 1,680 compared with the figure of 2,220 for Pump Scheme Strain. This lower yarn strength of Deltapine partly arises because of the higher figure for standard fibre weight per cm but more especially because of the low intrinsic fibre strength (as measured by fibre bundle strength on the Pressley Strength Tester)

If expansion of the Deltapine cotton had been made throughout the Nuba Mountains the character of the Sudan-American crop would have been completely altered Compared with American cotton from the U S.A of the same staple length, Sudan-American cotton gives yarns of consistently greater strength and this advantage serves as a compensation for the yarns generally tending to be rather neppier than those spun from cotton of the U S A. crop The Deltapine strain gives yarns weaker than most others spun from cotton of the U.S A. crop of the same staple length and if it had been adopted for replacement of the main crop then Sudan-American cotton would have suffered from a two-fold disadvantage and lost a considerable amount of its reputation

Strains for Equatoria

In Equatoria the first crops were grown from Pump Scheme Strain but breeding was carried out to obtain other types more suitable for the conditions in this part of the country.

The strain XA 129 arose as a single plant selection from Pump Scheme Strain It is of sturdier habit, more vigorous and of better yield and great ginning out-turn Although shorter than Pump Scheme Strain, XA.129 has given slightly greater yarn strengths, largely on account of its somewhat greater fibre strength. The strain has not been grown as a commercial crop since the middle of the war when cotton growing ceased on the eastern side of the Nile.

The strain 511 is a single plant selection from SG 85 (an introduction from Uganda and derived from the N 17 strain of Nyasaland Upland origin) made in Shambat in 1930 Repeated selection gave rise to substrains 511A, 511B, C, D and E, all of which were found by Knight to contain the B_2 factor for blackarm resistance This material was found to be of higher yield (in some cases the advantage amounted to 40 per cent) than Pump Scheme Strain The 511D type was adopted for general cultivation in the western parts of Equatoria. Samples of 511D tested at the Institute have been found to be about $\frac{1}{32}$ inch shorter than Pump Scheme Strain, a little coarser in standard fibre weight per cm., and of somewhat lower yarn strength The 511E strain gave slightly better agricultural results than 511D but was not up to the level of Pump Scheme Strain The advantage over 511D was insufficient to warrant the changing of the seed supply. The comparison of 511D with the BAR.SP.84 strain has been made above.

(*b*) IRRIGATED COTTON

At Zeidab, where the last surviving crop of Irrigated Sudan-American cotton is grown, the seed supply is composed of the Coker Wilds strain grown from importations from the U.S.A. This Wilds cotton replaced the Coker Delta Webber No 5 (and later imported sub-strains of this type) used at Zeidab by the Sudan Plantations Syndicate for a number of years. In recent seasons the annual production has averaged about 15,000 kantars, less than 4,000 bales of 400 lb The Coker Wilds cotton is blackarm susceptible but the low yields obtained in the Zeidab area do not arise from this but are caused by heavy losses following bollworm attack. The results of tests made at the Institute on the two top grades of commercial samples of Wilds cotton (sold under the "N" series of marks) are given in Table VI. These averages show that the cotton is of very long staple (effective length exceeding 46/32 inch compared with a typical figure of about 37/32 inch for the rain-grown crop of Sudan-American) and fairly fine with a standard fibre weight averaging about 180. Because of the increased length and fineness compared with, say, Pump Scheme Strain, the Zeidab cotton gives yarns of appreciably greater strength. In 40s count it has averaged a lea count-strength product of 2,400 compared with the figure of 2,220 for Pump Scheme Strain In carded yarns this irrigated cotton is suitable for commercial use up to about 64s count. Its long staple makes it suitable for use in combed yarns up to about 80s count, the combing not only increasing the strength of the yarn but affecting a marked improvement in appearance over that of the carded products Breeders and growers in the Sudan, and past users of the crop, may be interested in the comparison of the present Wilds type of cotton with other strains which were formerly grown on various irrigated areas.

The strain known as 513 was derived from selections made about 1931 by Trought from his own Punjab Early Strain from India. It was an early variety and out-yielded strains of later growth which frequently suffered heavier attacks of pink bollworm The 513 family of strains (several reselections of the original material have been made) contains the B_2 blackarm resistance factor By 1936, 513 had been adopted for commercial cultivation in the Berber district, although later it was partly replaced by the better quality XA 1129 strain described below Although 513 is of about the same length as Pump Scheme Strain and has a lower standard fibre weight per cm. it has given yarn strengths consistently a little weaker than those of Pump Scheme Strain. The cotton is irregular in staple containing a high proportion of short fibre but this is not sufficient to explain the low yarn strength which appears to be due to intrinsic weakness of the fibre.

From Pump Scheme Strain was selected the 514 strain from which breeders made successive re-selections 514A, B, C, D and E. Under irrigated conditions 514D and 514E gave higher yields than Pump Scheme Strain and were grown for a number of years in the Dongola district. The 514 sub-strains did not differ markedly in fibre characters. The material is longer and finer than Pump Scheme Strain with a yarn strength greater by an amount expected on the basis of this increased length and fineness. The exact figures of tests made at the Institute on material sent from the Sudan may be seen by reference to Table VI

The strain XA.1129 was derived by Bailey from an off-type in Meade cotton, seed of which had earlier been imported from the U.S A. XA.1129 gave a higher ginning out-turn than Pump Scheme Strain and under irrigated conditions gave an earlier and heavier crop The strain does not contain any resistance to blackarm disease By the 1939/40 season it was being grown in the Dongola area (where it displaced the 514 strain mentioned above) and on parts of the Government estates in the Berber district. XA.1129 is of about the same length as the 514 class of cotton but a little coarser (with a standard fibre weight of 189 compared with 174). Despite the greater coarseness XA.1129 gave yarns of greater strength than those spun from 514 cotton.

VII. IMPROVEMENT OF PLANT CHARACTERS AND LINT QUALITY

(*a*) Development of Resistance to Blackarm.

A description of the main manifestations of blackarm disease has been given in Section III. Because of the serious economic consequences of blackarm attack, this section is devoted to a more detailed account of the disease.

The genetical basis of blackarm disease has been described in a series of seven papers by R. L Knight (joint author with T. W. Clouston in the first of the series) published in the *Journal of Genetics* from 1939 onwards. In a memoir on "Breeding Cotton Resistant to Blackarm Disease" (*Empire Journal of Experimental Agriculture*, 1946, XIV, 153-174), Knight gives a résumé of the work in detail sufficient for most workers Other aspects are given in the annual "Progress Reports from Experiment Stations" of the Empire Cotton Growing Corporation Some of this work on the development of plant resistance is summarised below

With one or two exceptions of little commercial importance, *G. barbadense* (which includes Egyptian and Sea Island cottons) has been found to be fully susceptible to blackarm disease In the American Upland group (*G. hirsutum*) many types are fully susceptible, but others have been found to contain a single gene, which has been called B_2, conferring a considerable degree of resistance. Another gene, B_1, occurs in some types of American cotton but is much weaker than B_2 A third gene, B_3, has been isolated from *punctatum* cotton, (*G hirsutum*, var. *punctatum*, J B Hutchinson) and found to give important breeding results

In the publications by Knight referred to above it has been shown that these genes may be transferred to susceptible types by a back-crossing technique, and "Egyptian" strains of cotton carrying the main genes are now in existence.

The B_1 gene, fully dominant and originally obtained from a Uganda variety known as B 31, is of little value in the breeding of resistant American Upland cottons. It confers only a slight degree of resistance on fully susceptible Upland. Moreover, Knight has found that this gene is identical with a factor leading to a marked dwarf-bunched shape of plant, or else is linked so closely to another gene responsible for dwarf-bunched habit that the two appear impossible to separate. The secondary dwarfing effect associated with B_1 makes the use of this gene impossible in many American types of cotton In *barbadense* cottons, B_1 alone confers a certain but small degree of resistance to blackarm disease and may be used in breeding work without attendant trouble of dwarfing phenomena.

The fully dominant B_2 gene was also originally obtained from the B 31 Uganda cotton, but it has since been found to occur in a number of other Upland and *punctatum* cottons. The addition of the B_2 factor to susceptible Upland and Egyptian cotton confers a strong degree of resistance to blackarm attack. In *barbadense* material the synthesis of B_1 and B_2 in one strain gives increased resistance compared with that derived from B_2 alone.

The partially dominant B_3 gene alone confers marked blackarm resistance on a susceptible cotton, but its value both in Upland and Egyptian cotton lies in its additive effect, when used with B_2

The B_2 and B_3 genes are located on the same chromosome, but since the cross-over value is about 32 per cent. they may be readily isolated. B_1 is independent of the other two, being situated on a different chromosome.

The results of workers in the Sudan suggest that, in districts where blackarm attack is light or moderate, adequate resistance in Upland or *barbadense* material may be obtained from the use of B_2 Where attack is likely to be heavy, B_2 and B_3 together will be required, and in areas where severe conditions are likely to occur then the three genes together may be needed for *barbadense* cottons.

In Domains Sakel a programme is well advanced at Shambat for synthesising a type carrying B_1, B_2 and B_3. Tests have yet to be made on the lint of this material and consequently it is not yet possible to assess whether the complete transference can be made without effecting fibre quality. Nevertheless the results of work on the X 1730A type show that resistance can be introduced without any accompanying deleterious effect on the lint.

The final stage in the X 1730A programme is also envisaged to be a blackarm resistant type carrying the three genes It is possible that the adoption of blackarm resistant cotton, both in the case of X 1730A and Domains Sakel, for commercial growth throughout the various areas in the Sudan will not be made until the final integration has been made and successfully tried over a period The expansion of, say, first a B_2 type, followed later by one containing B_2 and B_3, and finally a third carrying all three resistance factors would provide a heavy load to the commercial seed propagation programme.

Details are given below of some of the intermediate stages in the blackarm resistance programme for X 1730A. The transference of the genes conferring blackarm resistance was carried out by Knight at the Shambat Station, and the material then sent to the Gezira Research Farm for multiplication, further selection and trial by Evelyn The blackarm resistant American types have already been mentioned in Section VI above

The decision to concentrate the first part of the blackarm programme on the X 1730A cotton was made because this type is grown mainly in the southern part of the Gezira, the area having the greater rainfall and previously liable to heavier attacks of blackarm than the drier northern region. The most advanced blackarm-resistant strain produced so far is that known as BAR X 1730L which is homogeneous for the B_2 gene. In a series of variety trials in the Gezira, from 1942/43 onwards, BAR X 1730L has given the same average yield as X 1730A. Superficially it would therefore appear that the addition of blackarm resistance has produced no beneficial effect on yield Other factors require, however, to be taken into consideration before drawing any conclusions. Stringent precautions are taken in the Gezira to exclude blackarm attack: the "filtering" of seed in the Gash, the uprooting and burning of crop debris and the method of seed disinfection have all been mentioned above. The date of sowing is delayed beyond what is considered desirable if danger of blackarm attack were not present. Consequently to avoid endangering the main crop, the variety trials have necessarily had to be conducted under conditions designed to exclude blackarm Moreover, the susceptible X 1730A used as a control has been grown from seed raised in the Gash, and the experimental BAR X 1730L has been grown from seed raised in the Gezira in the previous season It is generally considered that Gash-grown seed gives a better yield than Gezira-grown seed when grown the following season in the Gezira. It is therefore thought that the apparent lack of yield superiority in BAR X 1730L presents a biased picture of the potentialities of this type. Before the true situation can be evaluated it will be necessary to have trials on a larger scale, sowing the crop at an earlier date than the main crop, using Gash seed for sowing, and noting especially the effects on rare occasions when the normal precautions against blackarm occurrence are ineffective.

Fibre and spinning tests have been made on a range of 16 pairs of samples of X 1730A and BAR X 1730L sent in from 1942/43 to 1945/46. The average results of these tests are as follows·

	Effective length ($\frac{1}{32}$ inch)	Immaturity count (N-D)%	Fibre weight per cm.		Lea count-strength products	
			Mean	Standard	80s	100s
BAR X 1730 L	47·4	59–9	153	161	2300	1950
X 1730A ...	48 3	64–8	158	161	2300	1975

Although BAR X 1730L is of slightly shorter staple than X 1730A it has given yarns of equal strength, the slight expected drop presumably having been counterbalanced by other fibre characters.

In half of the comparisons BAR X 1730L and X 1730A were considered equal in yarn appearance, in seven cases X 1730A was ranked superior to BAR X 1730L, and only once was BAR X 1730L better than X 1730A. This difference in yarn appearance appears to be associated with the maturity of the cotton, in general X 1730A is more mature (maturity ratio=0·98) than BAR X 1730L (maturity ratio=0 95) In only one pair of the 16 comparisons was the BAR type found to be more mature than the susceptible type. In 11 cases X 1730A was appreciably more mature than BAR X 1730L with little difference in the remaining four cases

No standard spinning tests were made on BAR X 1730L in the 1946/47 season, but four small-scale tests gave strength results which favoured X 1730A rather than BAR X 1730L

The BAR X 1730L seed is derived from bulk expansion of material from the last stage (7th back-cross to X 1730A) of the blackarm transference programme. In a manner similar to the sifting of X 1730A, the BAR X 1730L stock has also been selected at the Gezira Research Farm for uniformity The purity selection obtained has been termed BAR X 1730L S1

The results of variety trials do not indicate any marked difference between the yield of BAR X 1730L S1 and that of BAR X 1730L or X 1730A Four samples of the selected strain (from comparative variety trials with X 1730A in the 1944/45 and 1945/46 seasons) have been tested for fibre and spinning characters with the following results.—

	Effective length ($\frac{1}{32}$ inch)	Immaturity count (N-D)%	Fibre weight per cm		Lea count-strength product	
			Mean	Standard	80s	100s
BAR X 1730L S1 ..	48 5	63–8	151	155	2290	1970
X 1730A . .	47 5	67–8	157	158	2250	1870

The limited number of results available to date suggests that the sifting of the BAR X 1730L stock has possibly resulted in the BAR X 1730L S1 selection having a staple slightly longer than X 1730A and a somewhat greater yarn strength A few small-scale spinning tests made on samples from the 1946/47 and 1947/48 trials gave yarn strength results which were a little greater for BAR X 1730L S1 than for X 1730A. In the earlier large-scale tests, two samples of BAR X 1730L S1 were more immature, and of poorer yarn appearance than the corresponding X 1730A material In the remaining two pairs of comparisons, BAR X 1730L was of better yarn appearance than X 1730A, in one case being of equal and in the other case of greater fibre maturity In the small-scale tests there was little difference in the yarn appearance of the two types.

Although the above fibre and spinning tests results are not sufficient to be conclusive and need to be substantiated by further work, they suggest that the BAR X 1730L S1 selection may prove to be of better character than the original BAR X 1730L stock

Material removed from the BAR X 1730L stock in the sifting programme by Evelyn was discarded when considered to be of inferior fibre quality, but carried forward when of good character, and later bulked to form an "improved selection", known as BAR X 1730L S2 So far only a few tests have been made at the Institute on this S2 material, and the results indicate little difference between it and the standard X 1730A type.

The strain BAR 4/5 is another blackarm resistant type of X 1730A derived by Knight and Evelyn by bulking up material from the 9th back-cross to X 1730A in the breeding programme involving the transference of the B_2 factor This strain should therefore contain a slightly greater proportion of X 1730A in its ancestry than BAR X 1730L, which was derived from the 7th back-cross to X 1730A

In a number of variety trials from 1944/45 onwards, the results of which are given in Annual Progress Reports of the E C G C , BAR 4/5 has given figures for seed cotton yield per acre which are generally somewhat lower, rarely significantly lower, than X 1730A. In these trials the ginning out-turn of BAR 4/5 has been found to be lower than that of X 1730A, resulting in the former having a lower lint weight per acre than the latter. This lower ginning out-turn of BAR 4/5 cannot have arisen as a direct effect of the inclusion of B_2, because BAR X 1730L has given higher figures than X 1730A for ginning out-turn. Presumably it has occurred by chance use of some low-ginning X 1730A material in the later stages of the back-crossing programme; it remains to be seen whether the multiplied seed stocks of BAR 4/5 are sufficiently variable to permit a higher-ginning sub-selection to be sifted out.

The results of fibre and spinning tests on 11 pairs of samples of BAR 4/5 and X 1730A, from variety trials from 1943/44 onwards, are summarised below

	Effective length ($\frac{1}{32}$ inch)	Immaturity count (N-D)%	Fibre weight per cm		Lea count-strength products	
			Mean	Standard	80s	100s
BAR 4/5 .	48 1	67–7	157	157	2320	1980
X 1730A .	48 1	65–8	157	159	2300	1940

Reference to the above Table indicates that there is little difference between the two varieties. The results of a few comparisons by small scale spinning tests on samples from the 1946/47 season confirmed that the yarn strength of BAR 4/5 was fully equal to that of X 1730A. In yarn appearance there has also been little to choose between the two cottons, sometimes one being superior and sometimes the other.

The strain BAR 4/11 contains both the B_2 and B_3 resistance factors, and represents a further step in the blackarm programme. The results of four tests in the 1945/46 season indicated that BAR 4/11 was a little longer and of slightly greater yarn strength than X 1730A. Four small-scale spinning tests made on material grown in the following season reversed this difference in yarn strength So far BAR 4/11 has tended to give yarns of poorer appearance than X 1730A No marked difference in fibre maturity has been noted, but the difference in appearance may be associated with a tendency for BAR 4/11 to be more irregular in staple than X 1730A The results of the few variety trials available indicate that the yield and ginning out-turn of BAR 4/11 are somewhat below those of X 1730A

The BAR 4/11 stock has not yet been through a "purity sifting" and consequently it is not possible to gauge its ultimate performance

In later work Knight has found *G sanguineum* (=*G. arboreum* race *bengalense*, Silow) to contain resistance to blackarm, and in the 1946/47 season the gene B_4 was successfully carried to the 8th back-cross stage in transference to a Sakel cotton It has been found that B_4 segregates independently of B_1, B_2 and B_3, and shows additive effects in conjunction with B_2 and B_3. Work on other strains showing blackarm resistance is in progress to see whether other major genes exist and may be segregated to provide additive resistance in commercial stocks

(*b*) DEVELOPMENT OF NEW PLANT TYPES.

It is not intended to give a detailed description of the remainder of the wide range of other plant work in progress at the Gezira Research Farm and at Shambat, but a brief account of some of the problems not mentioned elsewhere in this paper may be desirable for general interest and to present a more balanced picture of current research

The effects of leaf curl disease have been mentioned in a preceding section, and how X 1730A was successfully developed as a resistant variety compared with the susceptible Domains Sakel One project is to see whether it is possible to isolate a strain of Domains Sakel having the same satisfactory fibre quality as the present type, but showing marked resistance to leaf curl disease. It has been found that resistance genes exist, both in standard Domains Sakel and in the older selection known as Massey's Domains Sakel. A field technique has been developed which makes it feasible to select disease-free plants which transmit this character to their progenies. Much work remains before the eventual success or failure may be gauged.

Jassid attack has been seen to cause a marked decrease in crop yield and the most effective means of control so far found consist of spraying with insecticides. One satisfactory method of reducing the extent of jassids is the development of hairy types of plants, a method inaugurated by Parnell at the Empire Cotton Growing Corporation's Station at Barberton, South Africa, and which has had considerable success in Empire cottons of the American type. A fundamental study is being made by Knight of the genetics of plant hairiness and it has been shown that a main hairiness gene H_1 may be transferred from Peruvian Tanguis cotton to an Egyptian type (the strain known as NT 2) with little or no adverse effect on fibre quality This gene is now being re-transferred to Domains Sakel. An *arboreum* hairiness gene, H_3, has been isolated from *G. sanguineum* and is being transferred into a typical Sudan Sakel cotton so that its relations to H_1 may be studied. Further work now in progress at Shambat includes the transference of hairiness genes from other cottons into Sakel stock to determine their identity, and, if they are different, whether an accumulation can be built up in one type to give additive effects.

The better grades of Sudan Sakel generally contain less trash than the better grades of long-staple types from the Egyptian crop. Nevertheless, a type of Sudan Sakel containing even less trash than the present type (but with the same fibre quality and spinning performance) would be a decided economic advantage. The average grade would be higher and a crop of it would therefore sell at a higher average price.

One source of trash in seed cotton arises from the bracteoles below the boll. As the boll ages, these bracteoles wither, become brittle, and break up into pieces. Their fragments fall on to the seed-cotton in open bolls and so contribute towards lower grades and greater processing trouble for the spinner Attempts are being made to transfer a deciduous character, in which the bracteoles are shed before the main set of bolls open, from an American Upland cotton to Domains Sakel to see whether any improvement in grade is effected

Another line of work beginning to receive attention in the Sudan is alteration of the growth habit of the cotton plant. At some future date, when improvements have been effected in present methods, mechanical picking may prove desirable in some of the irrigated areas of the Sudan. The lay-out of the Gezira is particularly suitable for mechanical picking. The transference of "Egyptian Short Branch" and "Cluster" habits from other types to Sudan Sakel is being attempted to obtain a plant structure more suitable than the present types for mechanical picking

The above examples do not exhaust the programme of plant-breeding work of the Research Division which, among other things, includes the development of greater ginning out-turn, analysis of yields into components to determine which characters are important and may possibly be improved and selection for earliness in growth, a feature closely related to low plant node number.

VIII. GENERAL DISCUSSION AND FUTURE DEVELOPMENTS

This final portion of the paper presents a number of aspects relating to the course of development of cotton breeding and growing in the Sudan. One or two particular points have already been touched upon in the main text, and are only recapitulated or elaborated here for convenience. The main purpose of this section is not to provide a summary of the preceding treatment, but rather to outline the general position and to indicate which lines of development appear to deserve consideration It is hoped that the various views expressed may be of interest not only to consumers of the crop, but also to those formulating the broad aspects of future policy and to research workers responsible for the detailed work

The development of a new variety of cotton, and even effecting minor improvements in an established strain, necessarily takes several years. Cotton breeders must consequently keep ahead of current demands and try to foresee probable future needs We have shown above how geneticists and breeders in the Sudan are working on a wide range of problems, and that one of their aims is to obtain ultimately new seed stocks of improved plant character (by obtaining increased yields through modifications in plant resistance, habit, and structure) in which the character of the cotton lint is virtually identical with that of the present established commercial types.

This policy is largely based upon the fact that the two present Sudan Sakel types (the Domains Sakel or S qualities and the X 1730A or L qualities) are sufficiently distinct in character to present a different appeal to different spinners Domains Sakel finds its main use in fine yarns, frequently in counts of 100s or finer, and in medium counts where exceptional high strength is essential The X 1730A cotton is rarely used in very fine counts, but is suitable for use in counts up to about 80s in which it gives yarns of good appearance and of strength adequate for most purposes Where lustre and soft, silky feel are required, Domains Sakel is more satisfactory than X 1730A Where loftiness and firm handle are more suitable than silkiness, then X 1730A is preferred to Sakel.

Continuity of supply, and maintenance of quality at fixed levels are of commercial importance and enable the spinner to organise more easily the continuous production of standard types of yarn, and to feel confident that he will always be in a position to fulfil the future requirements of his customers for these lines without making intermittent drastic modifications in his pocessing The continued use of Ordinary West Indian Sea Island of the Montserrat type, in preference to some of the finer and stronger Egyptian types, provides an example of the value of maintaining trade confidence in stability of supply Apparently one reason why some such spinners use this cotton is that they believe it will continue to be grown with quality virtually unchanged long after some of the present super-quality Egyptian cottons (such as Amon and the already-disappearing Malaki) have vanished from the market.

It would be a relatively simple problem for breeders in the Sudan to produce, say, an X 1730A selection showing a desirable economic improvement in one particular plant character and which differed in lint quality from the present type By further work they might effect another improvement and issue a further supply of seed, one which showed another marked change in fibre length or fibre fineness That the harder road has been chosen, the method of improving plant character without effecting any noticeable change in average fibre quality, indicates that the authorities realise the desirability of maintaining the recognised fibre qualities of the types unchanged.

It is difficult for the breeder to estimate the likely future requirements of industry, the needs of which change with both fashion and fluctuations in national economy. He would need to make exceptionally accurate and inspired predictions to ensure that none of his work is wasted. The best that he can be expected to do is to develop a number of satisfactory cottons suitable for a number of uses, capable of being quickly developed for commercial growth should demands for the current type change Although many such cottons would never be grown for sale on the market, the need for them not having arisen, the work spent on their development would not be wasted It should be regarded as an insurance policy to cover likely emergencies.

One possibility is that there may be an increased demand for reasonably large quantities of super-quality types of cotton, appreciably better than either X 1730A or Domains Sakel To cover this contingency breeders in the Sudan are trying to develop a cotton of this type by straightforward selection work In the sieving of Domains Sakel stock for establishing the more uniform S_1 nucleus, a large amount of material was rejected as not being typical of the general crop. Some of the rejected material was considered to be of higher quality than the average and was developed in separate families. Material from six of the most promising families was tested at the Institute in 1944/45 and later bulked to form a selection known as Domains Sakel S_2. Further tests were made in the following season. The average results of the two groups of tests are summarised in the Table below.

	Effective length ($\frac{1}{32}$ inch)	Immaturity count (N-D)%	Fibre weight per cm		Lea count-strength product	
			Mean	Standard	80s	120s
Domains Sakel						
S_2 . .	50	65–9	136	139	2690	2170
Standard	48½	64–9	140	144	2630	2080

Compared with standard Sakel the S_2 selection is of longer and slightly finer fibre, and consequently of increased yarn strength. The difference in yarn strength was confirmed by a number of small-scale spinning tests in the 1946/47 season.

As yet the increase in quality of the S_2 selection is small, not sufficient to distinguish it as a new type. The work is being continued to see whether there is sufficient genetic variance in the stock to permit further selection pressure effecting a material increase in quality

Although high yarn strength may not always be essential it is certainly no defect Domains Sakel gives yarns sufficiently strong for many purposes Nevertheless any improvement in this direction would doubtless be welcomed by present users providing that other characteristics remain unaltered. Continued selection pressure for increased yarn strength normally results in a longer staple or a lower standard fibre weight per cm (or both) An appreciable increase in the length of staple of Sudan Sakel is not desirable because it would lead to greater trouble in processing and also make the cotton unsuitable for mixing with other long-staple Egyptian types. More over, the increase in length and the increased fineness would probably cause the cotton to have a tendency to nep, particularly in the inferior grades of lower immaturity. This trouble could only be overcome by increasing comber losses. These disadvantages would counterbalance the increased strength advantage. In a preliminary programme of work now being jointly tackled by cotton workers in the Sudan and at the Shirley Institute, it is hoped to avoid the above disadvantages by transferring high fibre strength from a wild species of cotton to Domains Sakel. If the project proves successful it will lead to an increase in yarn strength of Domains Sakel without any accompanying change in staple length or fibre fineness.

If marked changes in demand for Sudan Sakel occur in the future it is more likely that this will manifest itself in the need for a medium-staple Egyptian cotton (having a length intermediate between that of Ashmouni and Giza 7) rather than for a super-quality type approaching the best Sea Island. The research staff in the Sudan intend to see whether such a type may be developed to give adequate economic return in the various irrigated areas, and then to hold it in reserve until the need for it occurs.

From the economic viewpoint the growth of Domains Sakel appears to be at a disadvantage compared with that of X 1730A. The results of yield trials in the Gezira indicate that the lint yield of X 1730A averages about 20 per cent. more than that of Domains Sakel, the superiority being as pronounced in the North as in the South. Reference to current raw cotton prices shows that the premium in favour of Sakel over X 1730A is appreciably less than 20 per cent. Consequently it would apparently be more profitable to grow a crop of all X 1730A type instead of producing two varieties as at present. The problem is, however, not quite so straightforward as this, and it is necessary to consider the effects which abandoning Sakel would have on the demand for, and price of X 1730A.

We have already indicated that the two cottons are not interchangeable. If a crop of all X 1730A were raised, most spinners now using Domains Sakel for high quality mixings and fine yarns would necessarily turn to Egypt and purchase increased quantities of Karnak in preference to X 1730A. (A comparison of G3S and Karnak F.G + ¼, Type 155B, has been given in Section V. These two marks are generally sold at about the same price, the slightly lower trash content of the former being counterbalanced by the slightly greater yarn strength of the latter.) The Egyptian crop of Karnak is sufficiently large to supply spinners using Domains Sakel, and moreover could be increased if necessary. Consequently abandoning Domains Sakel and growing a large crop of X 1730A might result in a general weakening in the demand for the crop as a whole. The consequence of any such slackening in demand might result in a decline in price, sufficient to offset the increased yield. It is not improbable that the present lower profit on Domains Sakel may in effect be maintaining the relatively higher profit on X 1730A, because growing Domains Sakel prevents too much X 1730A appearing on the market.

One essential advantage of growing two types of Sudan Sakel in preference to one is that it removes the danger of having all one's eggs in one basket. Egypt is now producing a large crop of Menoufi, a cotton very similar to X 1730A. Moreover, still larger crops of the medium-staple Giza 30 cotton will be forthcoming in the future. This cotton offers a strong appeal to many spinners in the medium range of Egyptian yarns, and is more suitable than X 1730A for mixing with Ashmouni to raise the quality of mixings. The increased amounts of these two cottons will compete for some of the markets of X 1730A. If the effect is sufficiently strong to result in a slackened demand for X 1730A it will be possible to counter it by increasing the properties of Domains Sakel in the present crop to suit market needs.

It is clear that an increase in the financial return of Domains Sakel is desirable It is yet too early to judge whether the present advanced work of Knight on blackarm resistance will enable earlier sowings to be made and give materially higher yields and better grade, or to what extent current research on leaf curl, earliness, *etc*, will give marked advantages. The present need is for a cotton with a yield approaching that of X 1730A, including many of its other good agricultural features, but which has lint fully equal to that of Domains Sakel

At first sight it might appear feasible for plant breeders to carry out straightforward selection of X 1730A material in order to segregate such a type. The results of work along these lines in the past have given us no indications that it is possible to effect an appreciable increase in lint quality in X 1730A material Probably the most that would result from further work would be an "improved" X 1730A, having a lint quality between the present level and that of Domains Sakel There do not appear to be any prospects for such an introduction. The better grades of an intermediate type might be used by present consumers of the lower grades of Domains Sakel, leaving an unsaleable carry-over of these latter marks on the market. It would certainly not be suitable for users of the better grades of Domains Sakel The lack of demand for the intermediate type known as NT.2, which was tried a few seasons ago, lends emphasis to this point. NT.2 was selected as a leaf-curl resistant variety and a small crop was grown in the Gezira under the GN series of grades. Small quantities of the blackarm resistant type of NT 2 were grown in the Gash, where it was known as Barsak and sold under the KB series of grades. The cotton was a little coarser than Domains Sakel, gave yarns of slightly lower strength, and consequently offered little appeal to high-quality fine spinners Although the X 1730A and Domains Sakel are distinct in character, they are not sufficiently dissimilar to permit the easy marketing of an intermediate type.

Because of the degree of diversity of X 1730A and Domains Sakel it is possible that a new type, containing most of the desirable agricultural features of each but with the lint characteristics of Domains Sakel, might be evolved by hybridisation followed by intensive re-selection and possible back-crossing. Although this has not yet been tried in the Sudan on any large scale it is possible that it might help in solving the problem of balancing the high quality of Domains Sakel with its present relatively lower yield.

Sufficient has been said in the main text regarding the problems which confront the breeders of rain-grown American-type cotton Although marked advantages will be gained from the earliness of the new types, much work can still be done in increasing yield and developing new strains of about the present average quality but with increased fibre regularity and fibre maturity to reduce risk of neppiness

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By invitation from the Sudan Department of Agriculture and Forests, and by arrangements made through the courtesy of the Empire Cotton Growing Corporation, the author was enabled to spend some considerable portion of the 1945/46 season in the Sudan The major purpose of this visit was to acquire some first-hand knowledge of the difficulties and problems confronting cotton breeders and geneticists, in order to further investigations

of common interest jointly undertaken by these workers and the Shirley Institute.

Tours were made through several of the main cotton-growing areas to see the normal methods of cotton cultivation. The Director of Agriculture kindly made available the facilities of his department Much help was given by the Senior Inspectors of Agriculture in the different areas visited, and by many other members of the staff of the Department of Agriculture They freely imparted their long experience and discussed in detail the many agricultural problems confronting them

The Manager of the Sudan Plantations Syndicate in the Gezira wholeheartedly co-operated, and made it possible to study the picking of the crop, the grading system and the organisation of ginning Much valuable experience was gained by contacts through members of his staff, including Block Inspectors responsible for the cultivation of the crop and the manager of the Barakat Seed Farm in charge of maintenance and expansion of nucleus seed stocks

In particular it is desired to express the great appreciation due to Mr. R. R Anson (Chief Plant Breeder at the Gezira Research Farm and a member of the staff of the Empire Cotton Growing Corporation) Mr. Anson gave much detailed information on the work of his section of the Research Division, and on the past and present conditions in the Sudan from his long experience there At much inconvenience to himself he undertook most of the necessary touring arrangements in the Sudan, accompanied the writer over most of the Gezira and the Nuba Mountain cotton areas, and was largely responsible for the success of the whole visit.

At the Gezira Research Farm the Chief of the Research Division made all facilities available, and the various members of his staff freely gave up valuable time in their busy season in outlining their respective fields of work. Mr. S. H. Evelyn begrudged no time, despite being also heavily overloaded with additional work on crops other than cotton, in giving a comprehensive account of his large breeding programme of work on Sudan Sakel cotton.

At the Shambat Station, Dr R. L Knight, the Senior Economic Geneticist, not only thoroughly covered his own particular field of blackarm resistance and other branches of applied genetics, and imparted much of his long experience in the Sudan, but also spared himself no trouble by opening valuable contacts with various members of the Department of Agriculture visiting the headquarters in Khartoum Through these contacts it was possible to complete the picture by obtaining detailed knowledge of some of the areas which were not visited in person

Acknowledgement is also made to Mr C Underwood, of the Spinning Department of the Shirley Institute, under whose control all spinning tests have been carried out, and to the various assistants who have made many of the fibre measurements over a period of several years Finally the Raw Cotton Commission have always been most helpful in freely making available any needed samples of the commercial crop, and for ensuring that these were representative of their nominal grade and type.

As explained in the Introduction, it is hoped that the general references in the text, and in particular the acknowledgments above, will indicate where and by whom the various portions of the work on the development and growth of Sudan cotton have been conducted. In a paper of this nature it is, however, difficult to acknowledge adequately information gained by personal experience and by numerous contacts ranging from cotton breeders to the staff of the Raw Cotton Commission and cotton spinners, and apologies must be made for any inadvertent omissions. Some published information, additional to that quoted in the text and freely drawn upon in preparing this paper, is given in the list below.

REFERENCES

F W. Andrews The Effect of Leaf Curl Disease on the Yield of the Cotton Plant. *Empire Cotton Growing Review,* 1936, XIII, 287
R R Anson Anglo-Egyptian Sudan Cotton Production *Empire Cotton Growing Review,* 1947, XXIV, 169
M A. Bailey Leaf Curl Disease of Cotton in the Sudan *Empire Cotton Growing Review,* 1934, XI, 280
G C Dudgeon Egyptian Agricultural Products (Min of Agric, Egypt) No 3A, 1917.
G J Fleming Tokar *Sudan Notes and Records,* III, No 1
R Hewison Blackarm Disease in the Gezira. *Empire Cotton Growing Review,* 1932, IX, 276
R Hewison Some Factors affecting the Gezira Irrigation Scheme *Empire Cotton Growing Review,* 1935, XII, 25
A R Lambert New Sakel Strains in the Anglo-Egyptian Sudan *Empire Cotton Growing Review,* 1938, XV, 14
R. E Massey Blackarm Disease of Cotton *Empire Cotton Growing Review,* 1929, VI, 124
R. E Massey Studies in Blackarm Disease of Cotton. *Empire Cotton Growing Review,* 1930, VII, 185, 1931, VIII, 187, 1934, XI, 188
R. E Massey and F W Andrews Leaf Curl Disease of Cotton in the Sudan *Empire Cotton Growing Review,* 1932, IX, 32
T. Trought Cotton Growing and Breeding in the Anglo-Egyptian Sudan. *Empire Cotton Growing Review,* 1937, XIV, 197
Annual Reports of the British Cotton Growing Association
Annual Progress Reports from Experiment Stations, Empire Cotton Growing Corporation.

British Cotton Industry Research Association.

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33—EFFECTS OF STRAIN ON THE MICROSCOPIC STRUCTURE OF ACETATE RAYON

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I. GENERAL DESCRIPTION OF THE EFFECTS OBSERVED.

During an investigation of the manner in which cellulose acetate rayon fractured under the application of a simple tension, it was noticed that considerable change in the microscopical appearance of the filaments occurred This was subsequently found to be quite a general phenomenon for acetate rayon when broken or severely strained Two main distortions of the structure are produced; one is characterised by disruption of the surface, while the other has the appearance of an internal rupture As will be shown later, the latter, which is the more readily observable, is itself a modification of the surface effect The cracking of the surface is therefore to be regarded as the basic phenomenon, and will be considered at the outset

The surface of a broken acetate filament is depicted in Fig 1, it is seen to be covered with a large number of cracks, some in the form of minute individual centres and others spreading into lines of such centres. On the whole these lines are inclined to the axis of the filament as if part of some complex spiral pattern, and the general distance between them is about five to seven microns. In general this extreme disruption, though of greatest intensity near the break, can extend some five centimetres on either side towards the points at which the stress is applied.

The second effect to be discussed is illustrated on a broken filament in Fig 2, where the microscopical arrangement was such that internal detail of the filament was shown up, and surface structure eliminated It is seen that there extends down the filament, rather near to one edge, an axial band of markings which resemble cracks rather than cavities Finer detail, not resolvable with the optical equipment used, is also apparent This photomicrograph, although from a different filament of the same yarn shown in Fig 1, indicates that the distances between the more outstanding defects are approximately the same as those described previously. In fact if Fig 1 is examined closely, this internal effect can be seen as a series of large blurred dots running down the centre of the filament As this effect is associated with the strongly re-entrant parts of the filament it has been called the "cusp effect" Its presence is more readily observed than the surface cracking, and it extends back from the break to about the same distance Both phenomena usually occur together, although treatments establishing their independent existence have been found and are described below.

In its unbroken state of course, normal acetate rayon exhibits neither of these effects. Its surface is without structure and the only internal details are the axial lines denoting cusps

II. TECHNIQUES USED FOR THE OBSERVATION AND PHOTOGRAPHY OF THE STRAIN EFFECTS.

(a) Microscopical Equipment

For observation and study of the strain effects, especially the surface cracking, an optical system of reasonably high resolving power is desirable to reveal fine detail. For much of the work described here the authors found a 4 mm apochromat objective, fitted with a correction collar, to be particularly suitable. This was preferred on account of its high numerical aperture and its correction collar, which enabled a good image to be obtained in practically any desired plane of focus in a mount which, due to the bulk of the specimen, often possessed appreciable thickness. With the compensating eyepieces employed a range of magnification of 360 to 720 times was provided

(b) Technique for Rayon

Of the two forms of strain phenomena, surface cracking is the least readily observed. In mountants of refractive index similar to that of acetate rayon it is barely detectable, and to obtain satisfactory visibility of the surface a mountant of considerably higher refractive index is required Methylene iodide, either alone ($n=1\ 74$) or saturated with sulphur ($n=1\ 80$), was suitable for visual and photomicrographic work, and had no swelling effect on the rayon For photographic purposes only, an enhanced visibility of the effect was obtained by staining the filament in a saturated solution of Gentian Violet in cellosolve for thirty seconds. After a brief rinse in water the specimen was dried in the air. This technique was used in the preparation of Figs. 1 and 3, but it is stressed that no staining is required for visual work.

The cusp effect, from the standpoint of microscopy, can be considered as internal detail, and therefore any mountant of refractive index similar to that of acetate rayon and without swelling action will provide amenable conditions. Limonene, cedar wood oil, and liquid paraffin were all suitable No difficulties in the observation of the cusp effect have been experienced, and medium power dark ground illumination makes it particularly prominent.

(c) Technique for Film

Here the same mountants as those employed for observation of the cusp effect in yarns were found suitable. The microscope objectives were a 16 mm. achromat and an 8 mm. apocromat

III. DETAILED ANALYSIS OF THE STRAIN EFFECTS.

Except when stated otherwise the yarn used was 140 denier, 26 filament, unoiled cellulose acetate rayon, produced by Messrs. Lansil Ltd. Unnecessary interference with the observation of the surface occurs when oil is present on the yarn.

(a) The Influence of Extension

Samples of length 15 cm. were extended in a single-thread testing machine to 5, 10, 15, 20 and 25 per cent. elongation, at rates of 0·1, 1, and 5 cm. per second. For comparison, lengths were also broken by hand extension.

The strain markings on the broken samples, which were always more pronounced than those produced by elongation, showed the greatest intensity near to the break and diminished gradually as far as the points of application of the stress.

In the extended samples the markings were more restricted to a specific section of the yarn, generally near to the mid-point, and the cusp effect was always more definite than the surface cracking. No positive signs of either were present at extensions below 15 per cent., although faint traces of the cusp effect could be seen at extensions as low as 12·5 per cent. when dark ground illumination was used. It is felt that submicroscopic effects, probably observable with an electron microscope, are present below this extension.

In general, the higher the rate of extension the more marked are the strain effects, and in all subsequent experiments an extension of 25 per cent at 5 cm per sec was used After certain of the treatments described below the yarns would not extend to 25 per cent. and for these a hand break was used

Modifications of a simple extension such as those resulting from bending sharply or from application of a torque also produce the strain effects at places where elongation has occurred The surface cracking was also produced by rolling a weighted cog wheel along a yarn, the pattern showing clearly the regions of pressure caused by the teeth. As would be expected, since extension is here applied only to the outer surface, no cusp effect was found.

(b) The Influence of Age and Origin of the Yarn

Normal strain effects were exhibited by yarns whose ages varied between 3½ hours and 4 months Indeed one sample of unoiled rayon was broken only 15 seconds after spinning and still showed normal markings, although these did not extend far back from the point of fracture.

Commercial yarns manufactured by British Celanese Ltd., Courtaulds Ltd., E I du Pont de Nemours & Co , Eastman Kodak, and Société Rhodiaceta, spun between 1936 and 1947, were also found to give, when broken, the effects described above. Their filament deniers ranged from 1½ to 5.

With a sample of acetate rayon containing dispersed titanium dioxide the surface cracking was definitely present, but it was of course not possible to observe the cusp effect

From these observations the strain effects seems to be of quite general occurrence

(c) The Influence of Various Pre-treatments

When filaments were dried, either over phosphorus pentoxide at room temperature or at 110° C , a normal surface cracking was present after extension. The cusp effect was rather more pronounced than usual However, by soaking yarns in water to allow swelling, the effects after stretching were small in amount and the surface cracking was finer in texture. The results suggest that much of the latent strain in the filaments, which would result in heavy effects on extension, is removed When the surface only of the yarn was wet by immersion for three seconds in water containing a wetting agent the surface-cracking was again more fine in texture than that normally observed, and there was a greater amount than usual The strain has possibly been distributed more evenly over the surface by this brief wet treatment

Some attention was given to the influence of steam, samples being held in steam for two minutes and there broken by hand. At temperatures up to 200° C the cusp effect produced was small, but the surfaces of the filaments exhibited the most pronounced cracking. An example of this is shown in Fig. 3 which applies to a filament broken in steam at 100° C , the considerable depth of these cracks can be seen by the notches along the filament edge. It seems as if the filament is surrounded by a relatively inextensible skin which becomes rent under the tension. Clearly also these cracks are modifications of those shown in Fig 1 Breaking a filament immersed in warm water (at about 65° C) gives a result in between those of Figs. 1 and 3.

When yarns subjected to either the hot water or steam treatment are mounted in limonene and studied between crossed Polaroids the spiral nature of the surface cracking is more definitely revealed and is shown in Fig. 4. The pitch of the spiral is approximately the same for both samples, although that broken in steam appears of lower pitch due to the increased number of separate spirals present The spiral nature of Fig 1 (dry break) can similarly be demonstrated, but is not sufficiently pronounced for a reasonable photograph to be made A filament of flat cross section was used in order to eliminate any cusp effect

Comparison of Figs 1 and 3 reveals that the latter exhibits further surface detail not shown in the former This consists of a large number of transverse markings running almost at right angles to the filament axis. It is not easy to show how deeply these extend into the core of the filament, but a general examination in various mountants suggests that they are present only in the outer regions They are made more prominent by mounting in limonene and a photograph, in this medium, of the same field as that used for the steam-broken filament in Fig. 4 is shown in Fig. 5 This has been observed only in filaments broken in steam or in hot water and is less apparent with the latter treatment. Rather similar markings were found by A Herzog,[1] but these seemed to occupy the centre of the filaments, and moreover occurred on straining dry yarns. Herzog's results could not be reproduced, and it is thought that this may be due to differences in the rayon since his paper utilises results found on monofilament material in 1913

An incidental effect of stretching or breaking yarns in steam is that the parts lying in the steam become considerably delustred Filaments allowed to remain in the steam for a similar period of time (2 minutes), but not extended were practically unchanged.

Softening of the cellulose acetate was also produced by suspending yarns in cold acetone vapour prior to breaking. Very heavy surface cracking, limited to a few millimetres, occurred and was due perhaps to the great elongation possible No cusp effect was present. When the yarn was left 24 hours before breaking to permit evaporation of the acetone both effects were normal in intensity and extent.

In contrast to these examples some strain was deliberately produced in the surface of the filaments by delustring with 0 2 per cent. soap and 0 2 per cent phenol at 100° C for 1 hour, followed by washing and drying. The resulting filaments when broken exhibited extremely heavy surface cracking; it was of course not possible to observe the incidence of the cusp effect on account of the internal pitting which results from the delustring process.

A reduction of the extensibility of the filament surface was achieved by hydrolysing for 5 minutes in N/2 sodium hydroxide in half saturated sodium chloride solution, the latter being used to inhibit swelling. On breaking the washed and air-conditioned yarn the cusp effect was present normally, but the surface cracks were found to be quite wide openings due presumably to the lower extensibility of the cellulose surface compared with the cellulose acetate core of the filament On completion of the hydrolysis by overnight treatment the yarn was again broken and still exhibited heavy surface cracking This obviously means that the chain molecules themselves must be arranged differently in the surface from the inside, the inner ones being the less orientated. No cusp effect was present, and examination of the cross-sections showed that the deep re-entrant portions had fused together so as to exclude the sides of the cusp from being considered part of the surface.

(d) Removal of the Strain Effects

Attempts were made to seal up the cracks produced by the breaking of air-dry yarns. This course it was felt would give added information on the reasons for the incidence of the effects. Furthermore, C P. Tattersfield,[2] in a lecture has shown that the abnormally rapid hydrolysis of cellulose acetate yarn which had been subjected to extension or pressure could be reduced by certain after-treatments. Although the text of his paper was not available during these investigations an approximation to the treatments there recommended was made. Other after-treatments, not considered by Tattersfield, were included. In passing, it is considered here that the data of Tattersfield can be explained by the fact that the disrupted surfaces of strained filaments would permit rapid penetration of the hydrolysing agent

First it was found that neither dry heat for 20 hours at 110° C nor wet steam at 100° C. had any tendency to remove the effects However, treatments for five minutes at 130° and 200° C did modify the surface cracking to a very fine regular crazing and almost eliminated the cusp effect

After-treatment with saturated sodium chloride solution at 80° C was also studied This relatively low temperature was chosen to preclude delustring effects. After five minutes no alteration was observed, but in thirty minutes most of the surface cracking had been removed, and the cusp effect was lessened. It was treatments such as these that Tattersfield had recommended, and their success may be due to a gradual radial shrinkage of the yarn in the presence of the saturated salt solution.

Rather more success, as would be expected, was achieved by the action of acetone vapour. Times of exposure greater than ¼ hour were used and both the surface cracking and the cusp effect were removed entirely. Samples so treated for 20 hours were found to be fused together and clearly the surfaces of filaments left for shorter times would be sufficiently softened to allow incipient flow with resultant healing of the cracks.

(e) Observations on Cellulose Acetate Film

No detailed study was made with films and an exactly similar series of phenomena as that occurring with yarns was not expected since these effects clearly depend on the physical form of the samples and on differences in strain or in molecular disposition. In keeping with this view is the fact, recorded in the next section, that certain rayons other than from cellulose acetate can also exhibit analogous effects.

The film used was unplasticised, and was cast on a glass plate so as to have a final thickness of about 0 005 in. The effect of sharp and repeated flexing of this film is clearly shown in Fig. 6 The axis of the flex is shown by the incipient cracking and on either side of this is a broad band of fine dots. Even the edge of the film, which was cut with scissors shows these dots. Under higher power these dots are resolved into circular lenticular holes with the circular planes roughly parallel to the faces of the films It is important to remark here that this effect lies wholly within the thickness of the sheet, the surface of the film being, so far as observation at present can decide, entirely free from defects. Thus no parallel with the phenomena described for filaments can be drawn.

In order to observe the disposition of the dots within the sheet a sample was flexed three times each way through about 350°. The regions containing the strain effect were then measured by focussing down through the sheet progressively. Fig 7 shows the picture obtained, the two faces of the film being designated according to their dispositions during casting. It was not advisable to photograph the film in an edge-on position since the actual cutting of the film to form the edge would have resulted in a superimposed strain effect (see Fig. 8)

The widths of the bands are means of five series of measurements Subsequent tests have confirmed that the effect does not reach the surfaces, and that near to the glass surface the band of material free from these dots is always very narrow. The centre region, which is unaffected, would obviously suffer little elongation during bending and so is of no importance here Presumably the whole of the interior of the film is in a state that disrupts on straining The formation of this internal band may be considered to take place as follows. The film commences to harden slowly from the surface in contact with air and can move freely into a strainless configuration This freedom will be retained, though to a diminishing extent, over a finite thickness. Gradually, however, as the inside of the film solidifies it does so against an increasing restraint of the upper, previously hardened, layers, and is forced to shrink into a position of strain. Thus the nearer to the glass surface one goes the greater will be the strain, this is borne out by experiments in which sheets were bent only once and then not straightened out, when it was found that the dotted region was always more extensive and intense near to the glass surface of the film Indeed, when the glass surface was on the inside of the bend, that is, it was being compressed, some dotted appearance was produced near to it.

As an illustration of this progressive change in strain Fig 8 shows an edgeways view of a film clamped between metal plates and cut with a microtome knife. Incidentally the greater the sideways pressure during cutting the more intense was the effect. At the glass itself there must be a strong enough adhesion between the cellulose acetate and the glass to permit the permanent retention of the unordered molecular pattern of the solution when first cast. This increasing strain as one moves into the film is also manifested by the fact that the films always curl with the "glass side" inwards demonstrating the delayed contraction of the molecules formerly near to the glass surface

It is probable that the intense internal pitting observed when films are bent (which results in delustring at the fold) may be the reason for the whitening that is sometimes produced when electric cables coated with cellulose acetate insulation are strongly flexed.

(f) Observations with other Rayons

Several rayons, cellulosic and otherwise, were studied after they had been broken by hand. These observations are recorded without comment, but are considered more fully in the discussion as they materially substantiate the ideas there outlined

Viscose Rayon

Two samples of different manufacture showed a very faint trace of surface cracking, and this was of extremely fine texture. No cusp effect was present.

A third sample, of Italian origin, was similar with regard to the surface, but showed a wide band of internal cracking similar to, but even more extensive than that with acetate rayon On comparing the cross-sections of these three yarns it was found, however, that while the first two possessed a normal outline, consisting of sharp indentations and not cusps, the Italian rayon section showed a most exaggerated cusp running well into the centre of the filament.

H Reumuth[3] has recently observed fine surface fissures across the longitudinal axis of viscose after being laundered fifty times, and he suggests that they are indications of over-extension of the filaments. The effect was too faint to observe by normal methods and was detected, though with difficulty, by the new phase contrast microscope

Cuprammonium rayon

A faint trace of surface cracking showed very close to the break only No cusp effect was observed.

Nylon

No effect was present either on the surface or within the filament

Vinyon.

The surface cracking was similar to that appearing in acetate rayon, although the mountant (methylene iodide) had to be saturated with sulphur to prevent swelling of the fibre No cusp effect was seen, the filaments being of smooth, flat cross-section

IV. DISCUSSION

Although the main object of this work was to gain insight into the microscopical structure of cellulose acetate filaments the foregoing observations could be used as the basis of a test for distinguishing between chemical and mechanical breakdown In this connection the cusp effect would be the more easily observed, and for this purpose variations in the character of this effect need explanation Most often only a single line of cracks appears, occasionally there are two parallel lines, and infrequently three or more lines are observable. If an optical system of small depth of focus is used each row appears suddenly as the microscope is focussed down through the filament thickness Examples of these are given in Figs 9 and 10 where an objective with considerable depth of focus was employed in Fig 10 only. From their incidence as parallel rows within the filament they must occur along the re-entrant troughs which traverse the length of most acetate filaments. On focussing through a section these cracks can actually be observed flashing in and out of focus at the peak of the cusp The distance between the flashes was found to be identical with that measured between the dots when the filament was viewed in the entire Only the few well-pronounced cusps extending deep into the filament show the effect, the remainder, of incipient cusp-shape, being quite free In fact the cusp effect is really a surface phenomenon, but occurs at the junction between two surfaces where the mountant cannot penetrate With dehydration-mounting technique which gives penetration, visibility of the effect becomes extremely difficult Further proof of the correlation is that filaments of round or flat cross-section show none of these lines at all after breaking As would be expected a yarn which contains many filaments often exhibits all variations of the effect.

Recently a communication has been published by E V Martin,[4] in which rather similar effects are recorded Yarns were subjected to various amounts of drafting in hot air so that final strengths were much higher. Initially the yarn showed no internal defects whatsoever, but as the tension increased there appeared a row of cavities spaced several microns apart, and the number of these cavities in the row increased with the tension. A limiting tension was reached, however, beyond which new rows of cavities were formed until the filaments became delustred. Extrapolation of the results back to the unextended state showed that the cavity spacing at the point of natural result of the method of manufacture in which a concentrated solution of cellulose acetate in a volatile solvent is forced through fine orifices down a vertical chamber against a current of hot air When in the upper part of this chamber most of the dope stream will be liquid while its surface will be formation was about 0 4 micron. The author states that the rows generally occur near a wrinkle in the outer wall. Although obviously allied to the phenomena discussed here this effect is thought to be separate since the cavities are less than a tenth the distance apart of those recorded earlier in this paper

In closer connection with Martin's observations it is found that certain high tenacity acetate rayons contain axial streaks composed of many small dots These are present before breaking the yarn

The definiteness of the surface cracking as a true surface phenomenon is shown by the fact that a replica can be made by pressing a broken yarn with a hot iron into thermoplastic films such as benzyl cellulose, or plasticised ethyl cellulose or cellulose acetate, which exhibits all the surface markings of the yarn itself

The results of these investigations have led to the conclusion that the surface layers of any normal filament of acetate rayon differ from the inside in having a lower extensibility. This property can be understood as a a plastic semi-solid In the lower part the filaments are wholly solid due to the rapid evaporation of most of the solvent. Just below the orifice the whole winding tension of the yarn will effectually act on only a thin layer of solid material surrounding each filament, and the molecules in this will consequently become more orientated than when, at the later stage, the tension acts across the whole section For this to happen it is of course essential that the outer layers shall remain sufficiently plastic to be affected by the tension due to the continuous diffusion of solvent from the inside In melt spinning, as with nylon, this condition is not fulfilled, and different parts of the filament will set within a short time of one another Similarly in a wet spinning process such as is used in viscose rayon manufacture the outside layers are quickly coagulated and probably may not retain the necessary plastic properties With the example of the cusp effect shown with the Italian rayon an intermediate situation presumably arises, when, due to the very deep and narrow cusp, penetration of coagulant after the initial formation of the surfaces would be hindered and a plastic state retained It is of obvious importance that the only other rayon showing surface cracking similar to that with cellulose acetate should be Vinyon, which is prepared by an almost identical process.

In order to test these suggestions two experimentally spun yarns were obtained One was spun without draft by catching the filaments on a flat surface immediately they left the spinneret and moving the surface sideways as more yarn was laid on. In the other the yarn was given a very high draft, about double that normally used The first yarn, with an extensibility of well over 30 per cent., showed no cracking on breaking, while the second which broke at an extensibility of only 15 per cent , showed a marked effect despite the fact that normal yarn when extended to this amount was practically free from cracking.

The incidence of cracks in the form of a spiral is not new, and examples have recently been given for glass tubes when these contain any surface layer in a state of strain.[5,6] It must be presumed that this particular configuration is best adapted to the removal of the strain

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REFERENCES

[1] A. Herzog *Kunstseide*, 1934, 16, 128.
[2] C P. Tattersfield *J Text Inst*, 1948, 39, P541
[3] H Reumuth *Textile Research J*, 1947, 17, 69.
[4] E V Martin *Textile Research J*, 1947, 17, 512.
[5] J J. Hopfield *Nature*, 1946, 158, 582
[6] B N Clark and N. L Harris *Nature*, 1947, 159, 541.

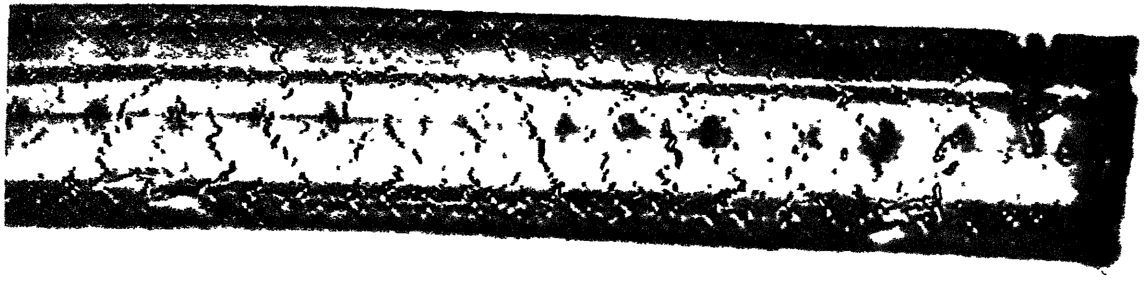

Fig 1 Surface of hand-broken filament ×1075, $n=1.74$, objective 4 mm apochromat
Specimen stained with Gentian Violet

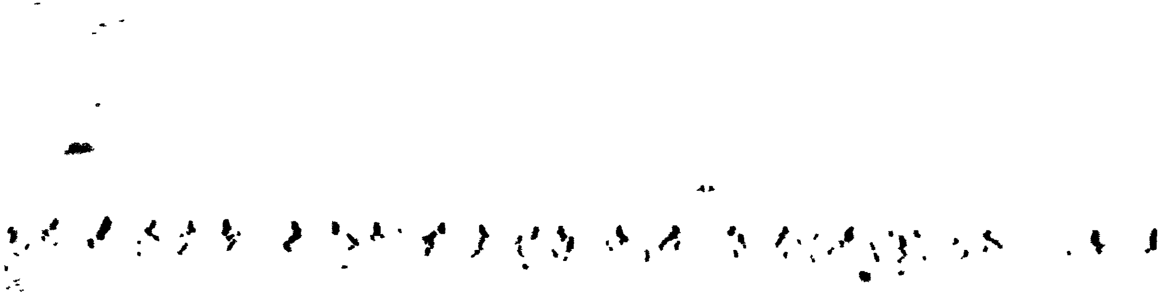

Fig 2 Hand-broken filament, re-entrant surface detail ×1075, $n=1.51$, objective 4 mm apochromat
Specimen unstained

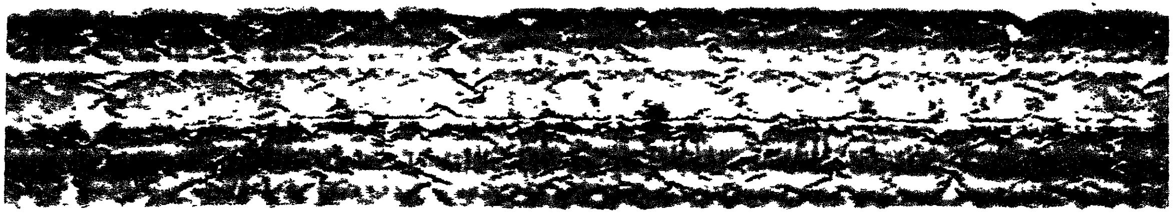

Fig 3 Surface of filament broken in wet steam × 1075, $n=1\ 74$, objective 4 mm apochromat
Specimen stained with Gentian Violet

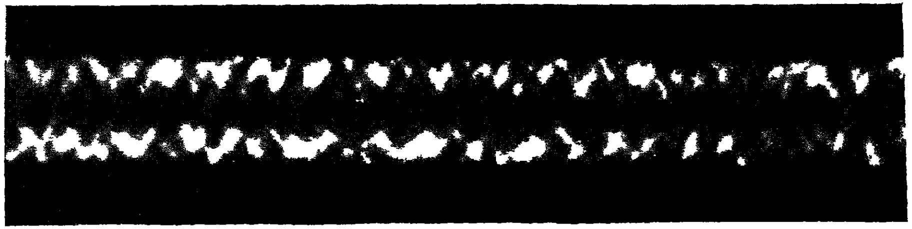

Fig 4 (*a*) filament broken in water at 65°C

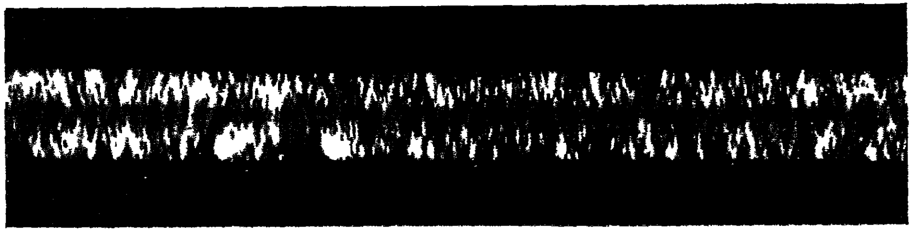

Fig 4 (*b*) filament broken in wet steam

× 500, n = 1 47, objective 6 mm achromat Both filaments photographed between crossed Polaroids

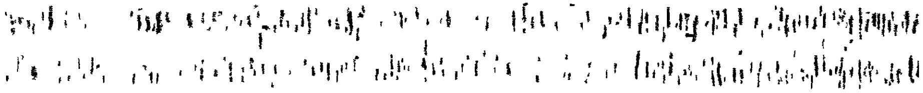

Fig 5 Filament broken in wet steam

× 500, n = 1 47, objective 8 mm apochromat

Fig 6

Unplasticised cast cellulose acetate film flexed six times through 350° ×125, $n=1\cdot51$

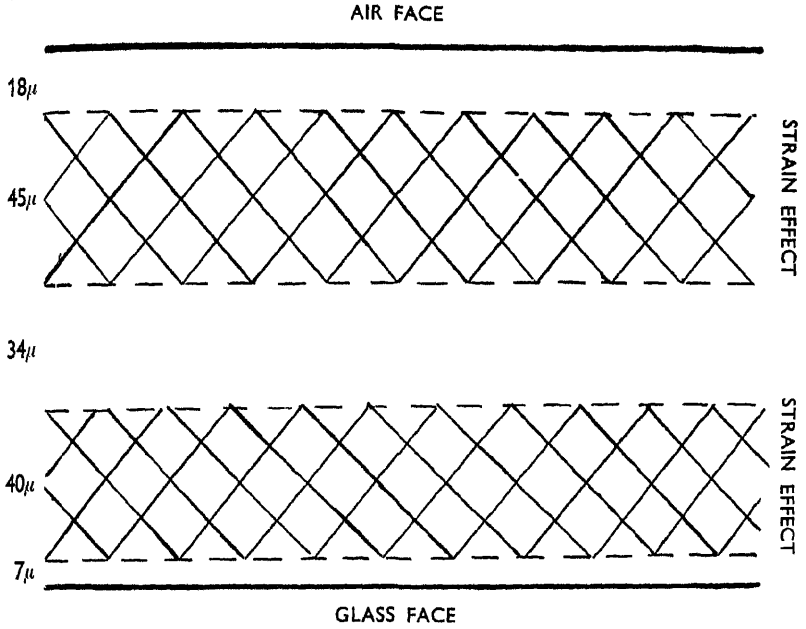

Fig 7
Diagrammatic section of flexed, unplasticised cellulose acetate film showing approximate position and extent of strain effects

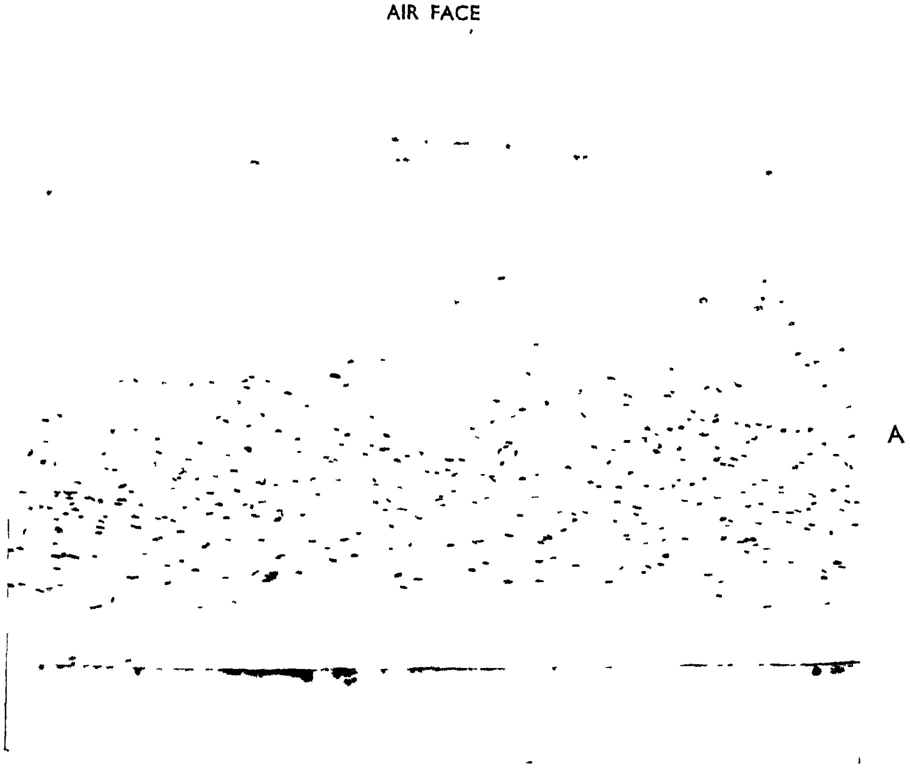

Fig 8 Section of cast, unplasticised cellulose acetate film clamped between metal plates and cut from A to B with knife edge at right angles to the direction of cut × 450, $n=1\cdot47$ objective 8 mm apochromat

Fig 9 Hand-broken filament, double cusp detail ×1075, $n=1\ 47$, objective 4 mm apochromat

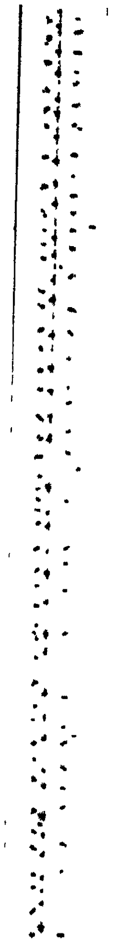

Fig 10 Hand-broken filament, triple cusp detail ×500, $n=1\ 51$, objective 16 mm achromat

34—THE VARIABILITY OF FINENESS OF MERINO WOOL FIBRE: ASPECTS OF ITS SIGNIFICANCE IN TOP-MAKING

By W R LANG

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SUMMARY

It is important for the woolgrower to know if the manufacturer requires his raw material within certain limits of fibre fineness variability or whether the frequent requests for uniformity in this respect have no real foundation The woolgrower judges his fleeces by visual and tactile examination of the staples and the staple formation at various fleece sites Information is available concerning the variability of fibre fineness in staples from a representative range of Australian merino wool The manufacturers' raw material may be regarded as compounded from staple components The woolsorter is the agent whose choice of suitable staples may improve the uniformity of the bulk submitted for manufacture Since the woolsorter relies on the crimp-fineness relationship of merino wool to guide his choice, hypothetical wool types of a given quality number have been compounded from staple components of a limited range of variability and the coefficient of variation of fineness of the resultant stock calculated arithmetically, the proportional representation of the components with respect to fineness and crimp being based on data already available These results have been used to assess the probable variability of the Noble combed top, due allowance being made for the removal of the noil These values have been compared with the variabilities of actual tops which have been prepared from "straight types", *i e* whose components are of one quality number and not a blend of two or more quality numbers Conclusions have been drawn concerning the effect of known variability of the component staples on the variability of the resulting top

INTRODUCTION

The fleece of the adult merino is composed almost wholly of fibres of one type, *i e* non-medullated, which are compactly grouped in tufts, known as staples or locks The normal staple has a wavy form, the waves being known as crimps Within one staple the fibres show a variety of thicknesses and lengths Duerden and Bosman[1] have shown that in the same staple, there is an almost perfect correlation between thickness and length and hence the uniformity of one indicates the uniformity of the other It is usual to express the variability of fibre thickness by means of the coefficient of variation, which, although not an ideal index, has not yet been replaced by a better statistical coefficient The coefficient of variation of fibre thickness of Australian merino wool ranges from as low as 10 per cent to approximately 30 per cent

The woolgrower, who is dependent on visual and tactile methods for assessing wool quality, is particularly interested in such fibre and staple characters as length, thickness and crimp He uses the staple crimp to assist him in assessing the fineness or mean thickness of the wool and while this is useful when dealing with large numbers of staples, it can be misleading in particular cases (Lang[2]) However, both the woolgrower and particularly the woolsorter, who prepares the raw material for manufacture, do place reliance on the crimp as a guide to fineness and this must be taken into account, when studying the composition of a stock or bulk of the raw material, which has been sorted, with the intention of obtaining greater uniformity of thickness and length, preparatory to manufacture

The woolgrower has often been advised to grow wool of greater uniformity The term "uniformity" has been used loosely in many of these requests and as will be seen below, it is employed in various senses In the scientific literature, the demand for greater uniformity is a reflection of the fear that the man-made fibres, with a greater control of the fibre dimensions, may therein obtain considerable manufacturing advantage over the comparatively variable natural fibre like wool. S G Barker[1] in the conclusion to "Wool Quality" has suggested that methods should be placed in the hands of the woolgrower "so that he may furnish the manufacturer with raw material of greater uniformity and higher average similarity in its characteristics" Bosman[1] has also expressed the opinion that the degree of fibre variability of wool is a significant factor in manufacture The manufacturer too, has often claimed that uniformity is not only desirable, but important in ensuring efficient worsted yarn production As an indication of his interest, he employs woolsorters to divide the raw material, which has already been classed on the stations or farms, into more uniform bulks suitable for his purposes Whether this sorting process really achieves what is intended appears to be unknown It seems highly likely that, in Australia at least, the manufacturer has no clear conception of the variations which occur in the greasy wool, nor whether his sorting practice is likely to improve the uniformity of the bulk or stock

In woolgrowing and woolbroking, the term "uniformity" is used in various senses, namely.—

1. Uniformity of fibre thickness along the staple

In this sense, it is essentially a request for soundly grown wool, as distinct from the "tender" or "unsound" staple It is a recognition of the need for a uniform thickness rate-of-production along each fibre This is generally assumed to be indicated by uniformity of the crimping along the staple but as shown by Lang,[2] this is not conclusive evidence in respect of individual staples Mean fibre thickness may change at successive stages along the staple without any corresponding change in the crimp and *vice versa*

2. Uniformity of mean fibre thickness in successive staples throughout the fleece proper, as distinct from the skirtings or more variable extremities, which are normally removed in wool classing

Among woolgrowers this is the meaning most frequently intended It is obviously desirable to grow fleeces with the minimum of thickness variation between the major sections of the fleece Again this is estimated visually and tactilely

3. Uniformity of fibre thickness of the composite fibres within the staple of fleece sub-unit

The variability of fibre thickness within the staple, indicated by the coefficient of variation, is known to lie between the approximate limits of 10 per cent and 30 per cent There is thus a considerable difference in the possible range of thickness between the more and less variable wools, with the same mean thickness

It is mainly with the third of these descriptions that this paper is concerned

Absolute uniformity of the raw material, besides being unattainable biologically is probably not desirable from the manufacturing standpoint It is also likely that the manufacturers' optimal requirement is not necessarily that of the sheepbreeder, who may be obliged to strive for greater uniformity of fibre thickness within the staple, to maintain an appearance which is attractive to the woolbuyer with his traditional subjective methods of assessment and to pay due regard to the genetical factors involved.

In woolsorting, the bulk of raw material for processing may be composed of wool of the same quality number or it may be blended from two or more qualities. In Australia the former practice is the more common and the material is referred to as a "straight type" This paper is entirely concerned with "straight type" sorting and the resultant combed product. After sorting, the wool is scoured and carded, any losses at this stage being ignored in this analysis Following the preliminary gilling operations, the Noble comb divides the top sliver from the "noil" or short fibres. The effect, if any, of the elimination of the noil must be considered.

The variability of fibre thickness of typical wool staples may be measured by well known microprojection methods If staple length, whose significance in manufacture has been studied by Stanbury,[5] is omitted from the discussion, of sorting, it can be assumed that the woolsorter is greatly influenced by staple crimp in his rapid assessment of the quality number of the merino fleece sub-unit when sorting a "straight type" Lang[6] has indicated the quality number-crimp relationship and[2] the crimp-fineness relationship in Australian merino wool. Thus for any quality number, the proportion in which the various crimp groups are likely to be represented and hence the probable distribution of mean fineness corresponding to these crimp groups may be derived In this way, theoretical "straight types" may be compounded, in which the staple is assumed to be the fleece sub-unit. By including staples of known variability, the variation of the resultant may be determined and its relationship with the components studied Finally by comparing data concerning the variability of actual Noble combed tops with these theoretical "straight types", valuable information on the significance of variability of thickness in the staple on topmaking is obtainable

The development of the argument will proceed in the following stages:

(1) It will be submitted that for "straight types" there is an upper limit to the coefficient of variation of fibre thickness in merino tops Daniels[7] has suggested 23 per cent.

(2) Assuming that any losses in worsted carding do not affect the variability of the stock, to examine whether any change in variability of fineness is caused by the elimination of the noil from the top in Noble combing. A typical merino tear, *i.e* top/noil ratio, of 8 has been chosen.

(3) A discussion of the methods of the woolsorter, in which, if the staple length be ignored, it becomes obvious that the woolsorter attaches great importance to the number of staple crimps per inch, the choice of typical frequency distributions of staple crimps per inch associated with the various quality numbers.

(4) From previous work it has been shown that for staples of the same number of crimps per inch there is a fairly wide frequency distribution of mean fibre thickness These have been extracted in tabular form.

(5) Since the coefficient of variation of fibre thickness may range from 10 per cent. to 30 per cent. approximately, staple components of the same coefficient of variation of fibre thickness have been taken and combined to make theoretical "straight types" according to the proportions suggested by the distributions of (3) and (4) above From (3) the crimp distribution for any quality number is known Each of these crimp groups is associated with a corresponding distribution of mean

thickness. Finally each component staple in this theoretical bulk is assumed to be of the same coefficient of variation Component variabilities of 15 per cent., 20 per cent and over 25 per cent. (coefficient of variation) have been chosen. The coefficient of variation of the resultant bulk has been calculated arithmetically and compared with the variability of the components

(6) By the combination of 15 per cent , 20 per cent and over 25 per cent. (coefficient of variation) components in different proportions, conclusions have been drawn concerning their relative significance in changing the variability of the bulk

ANALYSIS

1. Top and noil variability

An upper limit to the coefficient of variation of fibre fineness in merino tops in Australia, when a "straight type" is employed, is approximately 23 per cent. In large numbers of tops which have been measured in this laboratory over many years, the lower limit to the coefficient of variation has been approximately 17 per cent , with 72 per cent. of those examined lying between 20 per cent and 23 per cent This upper limit of 23 per cent has been confirmed by the experience of the Wool Industries Research Association (Daniels[7])

A question requiring an answer at an early stage in this study is whether the removal of the noil affects significantly the variability of the Noble combed top when compared with that of the carded sliver.

If a tear (top/noil ratio) of 8/1 is accepted as typical of merino tops, it cannot be considered that the removal of the noil greatly affects the variability of the top compared with the carded sliver For example, a 60s carded sliver as calculated from the fibre fineness distribution of an actual top and its noil, gives the following data, illustrating the conclusion

	Top	Noil	Carded Sliver (assuming a tear of 8/1)
Mean Thickness (μ)	23·7	21·6	23·5
Standard Deviation	5·19	3·98	5·10
Coefficient of Variation (%)	21·9	18·4	21·7

2. Woolsorting practice

Woolsorting, the first process of preparation in worsted manufacture, is a visual-tactile process in which there must be varied degrees of skill, depending on the experience of and the care taken by the sorter and on the conditions under which the work is performed Du Plessis[8] has noted that the great care taken in England forty years ago in sorting is no longer evident It is suggested here that this may have been for two reasons, either that experience has shown that highly sorted lines were not profitable compared with the less well sorted or that in effect, the efficiency of processing was not greatly influenced.

In sorting a "straight type" for topmaking, there are several practices obtaining in Australia, namely.

(1) The purchase of suitably classed types, which are used without further sorting

(2) Sorting in terms of the skirted fleece as the unit (Skirting is the process of removing the more variable extremities of the fleece)

(3) Sorting involving a smaller unit, which is best described as a "handful"

(4) Careful sorting in terms of the staple or lock as the unit

It is suggested that by studying the smallest sorting unit and its variability and theoretically combining together staples of given variability according to the general practices in sorting, much may be learned from the variability of the resultant "straight type". Experimentally it would be a tremendous task to gather together staples of like variability in sufficient quantity to make a conclusive manufacturing test The theoretical or arithmetical approach, although somewhat tedious, was therefore adopted. Before the hypothetical "straight type" may be compounded, there are several matters on which information is necessary:

(*a*) How carefully does a woolsorter restrict the staples sorted into the given type, with respect to such factors as crimp, staple length, *etc* ?

(*b*) What variability of fineness may be expected within the staple?

(*c*) What proportions, relating to crimp and mean fineness, are to be adopted in composing a theoretical "straight type"?

3. The woolsorter and staple crimp

Lang[6] had demonstrated the distribution of crimps per inch likely to be associated with any quality number This may be extensive or restricted in its range. In view of this, a number of sorted "straight types" was sampled and the distribution of crimp in 100 randomly selected staples recorded Two extreme cases are given in Table I

Table I

Frequency of occurrence of staples of various numbers of crimps per inch in two lots of sorted wool

Crimps (per inch)	Frequency Distribution of Staple Crimp (per cent) A	B
6	—	4
7	—	2
8	3	6
9	8	6
10	19	10
11	26	10
12	19	14
13	16	10
14	6	12
15	3	7
16	—	7
17	—	2
18	—	6
19	—	2
20	—	2

While it is obvious that in case A there has been some control of staple crimp during sorting, in case B it is difficult to understand why so wide a range of staple crimping has been allowed The selection for staple length in case B was fairly restricted, lengths varying from 7 to 11 cm. with 94 per cent in the 8-10 cm region, hence attention to staple length may have been the cause of the crimp variation.

It is obvious that woolsorters may vary considerably in their assessment of quality number, if staple crimping is taken as a criterion For calculation later in this paper it is necessary to make some choice of crimp distribution in the merino qualities 60s, 64s, and 70s, and an arbitrary choice has been made to use the distributions of the Melbourne group of quality assessors in Lang[6] (T260), which are given as percentages in Table II

Table II

Frequency of occurrence of staples with various numbers of crimps per inch in sorted wool (samples from all states : Melbourne assessment : 6 observers working as a team)

	crimps per inch							
	6–7	8–9	10–11	12–13	14–15	16–17	18–19	20–21
60s	7·7	56·6	30·6	5 1				
64s		7·5	42·5	35·0	7·5	7·5		
70s				7 6	23·2	54 0	7 6	7·6

4. Variability of fibre fineness within the staple

Since a common minimum fleece unit in practice is the staple, the range of variability shown therein is of prime importance in discussing this problem. The distribution of fibre fineness in the individual staples has been determined in the following way. Following Bosman and van Wyk,[9] samples were degreased in cold benzene and later mixed in ether to remove residual impurities. The benzene degreased staple was gripped between the forefinger and thumb, near the level selected for sampling and the cutting performed with scissors to give fibre snippings 0 3 mm to 0 5 mm in length. These short fragments were mixed thoroughly in ether in a petri dish and when "air-dry" were exposed in a desiccator for six hours before transferring to the standard atmosphere of 70° F and 65 per cent Relative Humidity for 24 hours They thus approached the standard atmospheric condition or regain from the dry side Clumps taken at random from the dispersed fragments in the petri dish were mounted using the medium known as Euparal 250 measurements were made on each sample, using a Bausch and Lomb microprojection unit giving 500 diameters magnification Two observers were used, each making 125 measurements, so that confirmation of their accuracy could be obtained. Other precautions to maintain accuracy have been noted by Lang[2]

In this way the mean and coefficient of variation of fibre thickness within a staple were found for 3647 Merino wool staples. The results are summarised in Figure 1 and Table III The top graph in Figure 1 shows the frequency distribution of within staple coefficient of variation for all those

Table III

Numbers of merino staples with various mean fibre thicknesses and the percentages of these having within-staple coefficient of variation above 20%

(1) Staple mean fibre thickness, μ	(2) Number of staples with mean shown in column (1)	(3) Percentage of the number of staples in column (2) with a within-staple coefficient of variation greater than 20%
15·0—15·9	72	40·1
16·0—16 9	149	34·3
17·0—17·9	227	28 2
18 0—18·9	329	20 5
19·0—19 9	409	19 3
20 0—20 9	474	19 8
21·0—21·9	539	15 0
22·0—22 9	437	14 2
23 0—23 9	368	20·1
24 0—24·9	280	17 8
25 0—25 9	168	17 7
26 0—26 9	109	16 0
27·0—27·9	86	24 6
	Mean Percentage of all groups . .	22·1

staples that had a mean fibre thickness of 26·0 to 26·9μ, and similarly for the other graphs. Table III gives the number of staples found in each of these mean fibre thickness groups and the percentage of staples having a within-staple coefficient of variation greater than 20 per cent.

5. Crimp-fineness relationship data

Lang[2] has presented data concerning the crimp-fineness relationship in Australian merino wool. If from Table II above it be arbitrarily assumed that in a 60s "straight type" the sorter may include 7·7 per cent. of 6-7 crimps per inch, 56·6 per cent. of 8-9, 30·6 per cent of 10-11, 5·1 per cent. of 12-13 (or indeed any other distribution) it is also necessary to know what fineness groups may be represented in the 6-7, 8-9, *etc.* staple crimp per inch classes. The relationship accepted herein is the set of frequencies found by Lang,[2] which is given in Table IV

Therefore in any "staple crimps per inch class" staples from the respective mean fineness groups and in the frequency indicated must be compounded to give a reasonably true result for that class.

6. Arithmetic simulation of "straight types" for topmaking

(*a*) *Selection of components*

It was decided to construct theoretical straight types for components of known coefficient of variation To this purpose suitable actual within staple distributions were selected as follows.

An actual fibre thickness distribution was chosen from those staples having a coefficient of variation between 15 and 16 per cent and also having a staple mean fibre thickness between 15 and 16μ, this distribution is given under the heading "mean fibre thickness 15μ" in Table V Similarly an actual distribution was chosen from those staples with a coefficient of variation between 15 and 16 per cent and staple mean fibre thickness between 16 and 17μ; this is given in the next column in Table V, and so on for the other staple mean fibre thicknesses.

This selection of distributions was then repeated from among staples with a coefficient of variation between 20 and 21 per cent, and again from among staples with a coefficient of variation greater than 25 per cent. Thus two more tables like Table V were built up. These tables are not given in full—only the part corresponding to the last two lines of Table V being given (in Table VI).

(*b*) *Variability in the respective crimp class intervals with the three sets of components*

Combining the crimps per inch classes 4-5, 6-7, *etc.* as in Table IV and deriving the distributions in the mean fibre thickness intervals and applying the data from the within staple frequency distributions for staples having a coefficient of variation between 15 and 16 per cent, the frequency distribution given in Table VII is obtained.

Similar tables were constructed for staples with 20-21 per cent. coefficient of variation and staples with over 25 per cent. coefficient of variation These are not given in full, only the resulting means and coefficients of variation are given (corresponding to the last two lines of Table VII) in Table VIII.

(*c*) *Deriving the* 60s, 64s *and* 70s *stock from the three sets of components*

It was decided to compose theoretical 60s, 64s and 70s from the foregoing data, using the distributions of crimps given in Table II. The resulting mean fibre diameters and coefficients of variation are given in Table IX.

Table IV
Observed percentage frequency distributions of mean staple fibre thickness within crimp classes

Mean fibre thickness of staple, μ	Staple crimps-per-inch classes									
	4–5	6–7	8–9	10–11	12–13	14–15	16–17	18–19	20–21	22–23
11										5·4
12							2·2		4·5	
13				0·5	0·5	0·6	1·6		4·6	5·6
14			0·5	1·2	0·6	1·6	2·4	9·0	9·0	11·2
15			1·0	2·1	3·3	2·8	3·2	6·0	27·4	22·3
16		0·3	0·6	3·5	8·6	4·8	9·6	7·0	13·8	22·3
17		0·3	3·5	6·0	8·4	10·0	9·6	15·0	9·2	16·6
18		1·8	5·5	9·5	12·6	14·6	17·5	27·0	9·0	5·6
19	2·0	3·6	10·1	11·8	13·3	12·4	16·7	15·0	9·0	11·0
20	2·0	8·0	14·7	14·2	15·5	14·6	11·1	9·0	9·0	
21	6·0	12·0	13·7	18·0	13·9	14·6	11·1	9·0		
22	5·0	11·9	13·0	12·2	9·3	10·1	11·8	3·0	4·5	
23	12·0	12·9	11·2	8·9	8·4	7·9	2·4			
24	9·0	15·0	10·9	5·4	3·4	3·4				
25	16·0	10·7	5·5	3·4	1·6	0·6	0·8			
26	8·0	7·7	3·8	1·9	0·3	1·0				
27	14·0	7·0	3·2	0·8	0·3	0·6				
28	6·0	4·9	1·0	0·2		0·4				
29	8·0	2·1	1·2	0·2						
30	2·0	1·5	0·2	0·2						
31	4·0	0·3	0·2							
32	2·0		0·2							
33	2·0									
34										
35	2·0									

Table V
Actual within staple frequency distributions of fibre thickness for staples with a coefficient of variation of fibre thickness of 15 to 16%

Class interval (μ)	Mean Fibre Thickness (μ)													
	15	16	17	18	19	20	21	22	23	24	25	26	27	28
8		0·8												
10	1·6	2·0	0·4											
12	7·2	3·2	2·8	0·8	0·4		1·6							
14	30·8	20·8	13·6	7·2	6·4	0·4	2·4	0·4	0·4			0·8		
16	31·6	33·2	26·0	23·6	14·4	11·2	3·6	2·4	0·8	0·4			0·4	
18	17·6	22·8	24·0	30·8	31·2	17·6	10·4	14·0	8·8	6·0	2·4	0·4	0·8	0·4
20	8·0	12·8	18·0	20·8	19·6	22·0	19·2	16·0	13·6	14·8	4·8	4·8	4·8	2·4
22	2·4	3·2	10·8	9·2	16·8	26·4	27·6	23·2	19·2	18·8	20·0	12·8	7·2	6·4
24	0·8	1·2	4·0	4·8	6·8	12·0	19·6	22·8	23·6	20·0	22·4	22·0	16·0	14·4
26			0·4	2·0	3·6	6·4	7·6	11·6	18·0	19·2	18·0	24·0	23·6	12·8
28				0·8	0·4	2·0	6·8	6·4	10·8	10·0	15·2	14·8	12·0	20·8
30						1·2	1·2	1·6	2·0	4·8	6·4	9·2	14·0	15·2
32					0·4	0·8		1·2	0·8	3·2	5·6	5·2	12·8	11·2
34								0·4	1·6	2·0	2·0	4·4	5·2	8·8
36									0·4	0·8	2·0	0·8	2·4	4·4
38											0·4		0·8	2·0
40											0·4	0·4		0·8
42											0·4	0·4		0·4
Mean thickness (μ)	15·8	16·5	17·8	18·9	19·3	20·9	21·8	22·5	23·6	24·3	25·7	26·6	27·3	28·5
Coefficient of variation %	15·6	16·1	16·3	16·0	15·8	15·5	15·8	15·0	15·0	15·7	15·8	14·7	15·0	15·0

Table VI

Mean fibre thickness and coefficient of variation for staples selected from (a) staples of 20 to 21% coefficient of variation, (b) staples of over 25% coefficient of variation

	Mean fibre thickness group													
	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Mean fibre thickness (a)	15 9	16 6	17·6	18 9	19 2	20·5	21·5	22·6	23·2	24 3	25 4	26 2	27·3	28 0
Coefficient of variation (a)	19 9	19·7	20 5	20·5	20 6	20 5	19 8	20 1	20·1	20 4	20 4	20 7	20·4	20 8
Mean fibre thickness (b)	15 7	16 4	17 1	18 1	19 8	20 3	21 9	21 7	23 4	24 3	25 4	25 1	27·6	28·2
Coefficient of variation (b)	26·9	25 3	33 4	26 7	26 6	26 0	25 3	25 8	28·8	33 9	26 3	30 5	25 6	24·6

Table VII

Percentage frequency distributions showing total variation of fibre thickness within a crimp class where within staple coefficient of variation is 15 to 16%, *i.e.* results of Tables IV and V combined

Fibre thickness interval (μ)	Crimps per inch classes									
	4–5	6–7	8–9	10–11	12–13	14–15	16–17	18–19	20–21	22–23
8					0 1		0 1	0 1	0 1	0 2
10			0 1	0 2	0 3	0 2	0·4	0 4	1 0	1 2
12	0 1	0 2	0·5	1 0	1·2	1 2	1 6	2·1	4 1	4 5
14	0·4	0 9	2 6	4 7	6 5	6 2	8 9	11 3	19·4	21 7
16	1 0	2 9	6 9	10 5	13 9	13 5	17 1	20 9	25 9	28·7
18	4 5	8·6	13 7	16 8	19 2	19 2	21 7	23 8	21 2	22 1
20	8·2	12 5	15·7	17 0	17 5	17 6	17 4	17 5	13 4	12 7
22	14 6	18 5	19·5	19 0	17 4	17 5	15 3	12 8	8 3	5 9
24	18·7	18 9	16·3	14 2	11·8	12 0	9 5	6 6	4·0	2 3
26	16 6	14 7	11 1	8 3	6 5	6 6	4 5	2·7	1 6	0 6
28	13 7	10 1	6 8	4 9	3 6	3 7	2 3	1 3	0 6	0·1
30	8 5	5 1	2 9	1 6	1 0	1 1	0 6	0 3	0 2	
32	6 5	3 7	2 0	1 0	0 6	0 7	0 4	0 2	0 2	
34	4 1	2 2	1 1	0 5	0 3	0 4	0 1			
36	2 0	1 0	0 5	0 2	0 1	0 1				
38	0 7	0 3	0 1							
40	0 3	0 1	0 1							
42	0 2	0 1	0 1							
Mean thickness μ	25·7	24·0	22 3	21 1	20 3	20·4	19 4	18·6	17 4	16 9
Coefficient of variation %	18·0	18·6	19 9	19 7	19 9	19 8	19 6	18 8	19 5	17 3

Table VIII
Resultant fibre characteristics of crimp classes when within staple coefficient of variation is (a) 20 to 21%, (b) over 25%

	Crimps per inch									
	4–5	6–7	8–9	10–11	12–13	14–15	16–17	18–19	20–21	22–23
Mean thickness (a)	25·4	23·7	22·1	20·9	20·1	20·2	19·4	18·6	17·4	16·8
Coefficient of variation (a)	22·8	23·1	23·9	23·8	23·6	23·8	23·1	22·6	23·1	21·3
Mean thickness (b)	25·6	23·9	22·1	20·9	20·1	20·2	19·3	18·4	17·3	16·7
Coefficient of variation (b)	28·8	29·8	30·3	29·7	20·0	30·0	29·3	28·2	29·0	27·1

Table IX
Fibre characteristics of straight types compounded from staples having various within staple coefficients of variation of fibre thickness

Within staple coefficient of variation	Quality number			
	60s	64s	70s	
15—16%	22·0	20·7	19·5	Mean fibre thickness, μ
	20·2	20·0	20·0	Coefficient of variation of fibre thickness
20—21%	21·7	20·6	19·4	Mean fibre thickness, μ
	24·2	23·9	23·4	Coefficient of variation of fibre thickness
over 25%	29·9	20·5	19·2	Mean fibre thickness, μ
	30·7	29·7	29·4	Coefficient of variation of fibre thickness

(*d*) *Resultant "stock" derived from proportions of components of different variabilities*

The next question that arises concerns the calculation of theoretical "straight types" of 60s quality from different proportions of components drawn from the 15-16 per cent. (F_{15}), 20-21 per cent. (F_{20}) and over 25 per cent (F_{25}) coefficient of variation results derived above. These are given in Table X.

(*e*) *The effect on the resultant "stock" of substituting* 10 *per cent of a more variable component of a range of mean thicknesses*

It is interesting to see the effect of substituting 10 per cent of an over-25 per cent.-coefficient-of-variation-component in a resultant "stock" compounded from components of 15-16 per cent. coefficient of variation. It must be remembered that the effect of such substitution is dependent on the mean fineness of these components compared with that of the original "stock" in which they are substituted. As the mean of the substituted fraction passes from one extreme of the range to the other, it is found that the coefficient of variation first decreases to a minimum and then increases.

Table X

Fibre characteristics of straight 60s tops compounded of various proportions of components having different within staple variability

Proportions of components			Coefficient of variation, %	Mean fibre thickness, μ
F_{15}	F_{20}	F_{25}		
10	0	0	20·2	22·0
8	2	0	21·1	21·9
6	4	0	22·1	21·9
4	6	0	23·0	22·0
2	8	0	23·4	21·9
8	1	1	22·4	22·2
7	2	1	22·7	22·2
6	3	1	23·0	22·2
5	4	1	23·2	22·2
4	5	1	23·6	22·1
3	6	1	23·9	22·1
2	7	1	24·1	22·1
1	8	1	24·5	22·0
7	1	2	23·4	22·2
6	2	2	23·6	22·2
5	3	2	23·8	22·2
4	4	2	24·1	22·2
3	5	2	24·5	22·1
2	6	2	24·9	22·1
1	7	2	25·0	22·1

The change in the resultant coefficient is significant and not negligible. This is shown by the figures in Table XI, which gives the coefficients of variation of mixtures of

90 per cent of stocks of three qualities compounded from staples with within staple coefficient of variation = 15-16 per cent.

10 per cent of a stock whose mean fibre thickness is given in the first column and which has (*a*) 20-21 per cent within staple coefficient of variation, (*b*) over 25 per cent coefficient of variation.

Table XI

Per cent. coefficients of variation of resultant stock (see text)

Mean thickness of the 10% part μ	10% part has within staple coefficient of variation 20—21% and quality No of 90% part is 60s	10% part has within staple coefficient of variation over 25%		
		Quality No of 90% part. 60s	64s	70s
15	22·0	22·6	21·8	21·4
17	21·3	21·8	21·4	20·9
19	20·7	21·1	20·6	20·7
21	20·4	20·6	20·3	20·8
23	20·0	21·1	21·3	21·9
25	20·8	21·6	21·9	22·8
27	21·4	22·1	22·7	23·9
Coefficient of variation of the 90% part without addition of the 10% part	20·2	20·2	20·0	20·0
Mean fibre thickness of the 90% part, μ .	22·0	22·0	20·7	19·5

(f) Coefficient of variation of resultant "stock" if all survey samples are combined in their various crimp classes

The coefficients of variation for the frequency distribution of fibre thickness for the "crimps per inch" classes on the Merino Survey of Lang[2] (2,416 samples) determined as before are given in Table XII. If the respective distributions are combined in the proportions of Table II for the three quality numbers 60s, 64s and 70s, the coefficients of variation for the resultants are 23·2, 23·4 and 21·7 per cent., respectively.

Table XII

Coefficients of variation of fibre thickness within crimp classes

Crimps per inch	Coefficient of Variation, %	Mean fibre thickness, μ
4—5	24·8	27·0
6—7	23·9	23·8
8—9	22·8	22·1
10—11	22·5	20·9
12—13	23·1	20·0
14—15	21·9	19·9
16—17	21·3	19·6
18—19	20·0	18·2
20—21	19·8	18·2
22, 23, 24	20·9	16·7

DISCUSSION

The first assumption that has been made is that a "stock" or "straight type" is composed of staples of varying degrees of uniformity. In classing, some of the shorter and less desirable portions of the fleece are skirted off, but usually the wool arrives in the sorters' hands in fleece units. These may be sorted in fleece units or, as in the most careful practice, be divided into staple or near-staple units. Let the more careful practice be assumed.

The woolsorter may be charged with the responsibility of obtaining a uniform line, with respect to staple fineness or staple length or both. Thus he may emphasise length at the expense of fineness or *vice versa*. As indicated in Table I, section 3, his performance as measured by uniformity of staple crimping is sometimes rather surprising. In assessing merino fineness, crimp is used as a major guide. It is suggested that the woolsorters' performance in reducing the variability of the raw material by careful sorting, is very much taken for granted by the manufacturer. It is true that he serves a very useful purpose in ridding the raw material of staples containing certain contaminants or in assessing the extent of such contaminants. For example, in the manufacture of white knitting yarn, the removal of every sign of brand-contaminated wool is essential. However, in respect to the reduction of variability of the raw material, it is submitted herein that he suffers certain very serious disabilities. In the first instance, if he depended on crimp to guide him in establishing fineness, and if he selected staples of a restricted range of crimping, since Lang[2] has shown that in handling large numbers of staples there is a correlation of crimp and fineness, he will to some extent restrict the range of fineness, but in practice the woolsorter seems not necessarily to be able to select to a restricted crimp range. A wide variety of crimp ranges may be detected in moving about the Australian sorting community. While some of this is obviously careless sorting, the distribution B (Table I) was the work of three serious-minded sorters working in almost complete silence. They stated that they were not wittingly sorting for length alone, but were trying to get a reasonably uniform

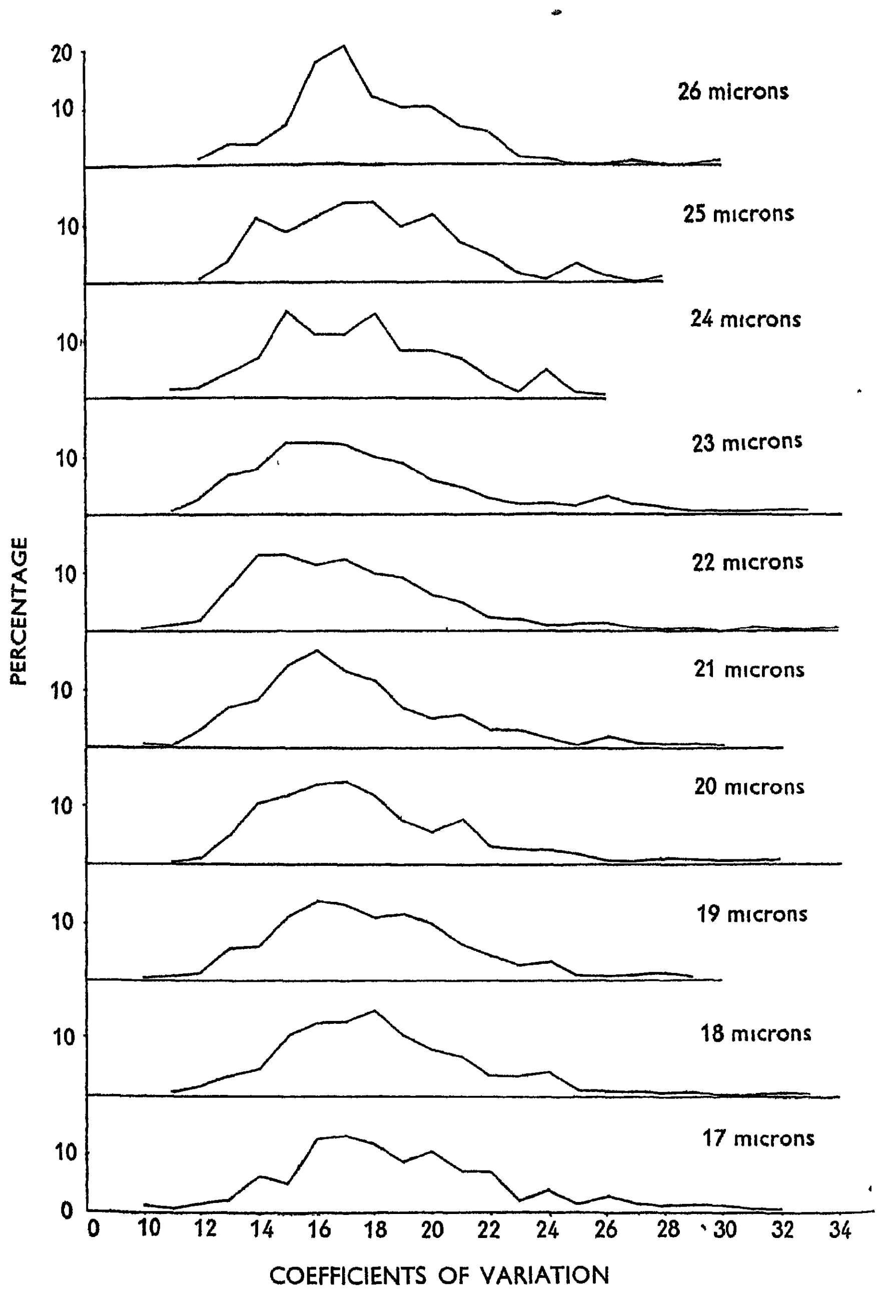

Fig 1 Frequency distribution of coefficients of variation within a staple for various values of the mean fibre thickness within the staple

fineness and length. Distribution B is typical of their usual result. If such sorters are not selecting to a limited range of crimp as a guide to fineness, and if as Lang[10] has illustrated, visual discrimination of fineness to less than 3 microns, with the best of lighting and backgrounds and conditions for comparison, seems impossible, then tactile assessment alone is responsible. If, however, when these staples are measured for fineness, the mean thicknesses vary according to the crimp-fineness relationship table, it would seem to indicate that the woolsorter is working somewhat uncritically. The laws of probability seem to affect the proposition as seriously as the sorters' powers of assessment.

To return to the staple units, their coefficient of variation may range from 10 per cent. to approximately 30 per cent. (see Fig 1). A question which immediately arises is, what kind of variability would be obtained if all the wool samples in any one crimp group were combined Table XII shows that the coefficient of variation for the groups which occur most frequently, namely 4-5, 6-7, 8-9, 10-11 and 12-13 crimps per inch, are around 23-24 per cent. As the crimps per inch increase, the coefficient of variation drops to the 20-22 per cent range If then these crimp groups be combined in a typical proportion to represent 60s, 64s and 70s, it is found that the resultant coefficients of variation are 23 2 per cent., 23·4 per cent. and 21·7 per cent., which shows that to keep within the 23 per cent. limit requires the elimination of but few variable samples in the 60s and 64s and none at all in the 70s. While this appears to minimise the significance of variable wools, it must be remembered that such distributions include large numbers of very uniform staples as well as the more variable representatives of the class. Experience in measuring large groups of staples from different clips and from different flocks suggests that the distributions quoted for groups combining samples from Australia-wide sources are not necessarily typical of different clips or flocks. Some flocks are almost entirely composed of sheep from which test samples average well below a 20 per cent coefficient of variation On the other hand, there are a number of merino flocks, usually among those producing 60s types whose average coefficient of variation in representative staples is around the 25 per cent mark If a stock be made from a large lot from such a source as the last mentioned, it would, in the light of the calculations of section 6, have an over-all coefficient of variation higher than a stock compounded from a source of the first mentioned type. In Australian manufacturing practice, it is not uncommon to work on straight-lines from limited sources, whereas it is less common overseas. Since the former practice does obtain, it behoves the breeder and flock master to take notice of such a fact, so that if there is any unfavourable significance in using wools of high variability, his clip does not achieve manufacturing notoriety as a poor spinner.

A " straight type " sorted from a number of sources will tend to approach the over-all variabilities reported in Table XII. However, the best advice to the breeder on this subject must take account of the first mentioned practice, which may reveal unfavourably a clip of greater over-all variability. Probably only a minority of clips are involved, but in terms of sheep numbers, these represent some millions of sheep in the Commonwealth of Australia and the problem is therefore not unimportant.

To gather information on the resultant variability of a straight type composed from staples of the same coefficient of variation, three sets of actual frequency distributions were chosen (Tables V and VI), representing 15-16 per cent., 20-21 per cent. and over 25 per cent. coefficient of variation. These were first compounded in the proportions suggested by Lang's[2] crimp-fineness relationship (Table IV) to give frequency distributions in the main crimp classes. The three sets of results are given in Tables VII and VIII. At this stage, it was necessary arbitrarily to select a typical crimp distribution for 60s, 64s and 70s, sortings. As a basis for this an assessment by six Melbourne experts working as a team and giving one of the more restricted distributions in terms of crimp (Lang[6]) as shown in Table II, was selected. The distributions of Tables VII and VIII were then recomposed in the proportions given in Table II, giving the resultant coefficients of variation for the completed "straight type" sorting shown in Table IX It will be seen from Table IX that for components of 15-16 per cent coefficient of variation, the final coefficients of variation for 60s, 64s and 70s are 20·2, 20·0 and 20·0, respectively, that is, an increase of 4-5 per cent in the coefficient of variation of the resultant over that of the components For the components of 20-21 per cent. coefficient of variation the increase is approximately 3-4 per cent. and for the components of over 25 per cent coefficient of variation, approximately 3-5 per cent. In these three cases the resultant stocks are of the order of 3-5 per cent. greater coefficient of variation than the ingredient staples

It has been noted that the coefficient of variation of a "straight type" merino top is not usually higher than 23 per cent It has been indicated that the elimination of the noil from the original stock cannot greatly change the variability and hence for the purposes of this paper, its removal has been ignored as not significant to the main argument.

The first conclusion in this aspect of the problem is that in the purely hypothetical case of a stock from components of identical variability, the variability of the whole, expressed as a coefficient of variation, is greater than that of the single components. This hypothetical case, however, gives useful general guidance.

It is obvious that for those tops whose coefficient of variation lies below 20 per cent., as some do, the components must have been of lower variability on the average and if ingredient staples of over 20 per cent. coefficient of variation were included, then a proportion of very uniform staples must also have been included to offset the effect of the very variable ones on the variability. It is interesting to note too that if 15-16 per cent. coefficient of variation components cause a final stock to rise to approximately 20 per cent. coefficient of variation, then there is no great scope for the addition of staples of greater variability, as their presence must be offset with components of coefficients less than 15-16 per cent. and Figure I shows that there is a lower limit of 10 per cent to these possibilities.

In Table X, the effect on the variability of a 60s compounded of staples of 15-16 per cent. coefficient, by substituting increasing fractions of 20-21 per cent. coefficient and also of "over 25 per cent." coefficient is recorded. A combination of 40 per cent. of F_{15} (using the nomenclature of Table X) and 60 per cent. F_{20} brings the final coefficient to 23 per cent. which for for the purposes of the paper, will be regarded as the upper limit in general practice. A second conclusion may be inferred here, namely, that the staples of F_{20} combined with proportions of F_{15}, which might be reasonably expected to occur, are relatively safe, if the limit of 23 per cent. for the resultant is not to be passed.

On the other hand, the presence of 10 per cent of F_{25} is responsible for the significant increase of the resultant coefficient towards the limit with large proportions of F_{15} still present Any stock with a coefficient below 23 per cent. cannot afford to have 10 per cent. of F_{25} without a large proportion of F_{15} The presence of 20 per cent. of F_{25} with the minimum of 10 per cent of F_{20} and the rest of F_{15}, has passed the suggested limit A third conclusion suggested by this is that a clip or lot with 10-20 per cent of staples of over 25 per cent. coefficient of variation would be likely to cause a resultant over the 23 per cent. limit. Hence F_{25} components need to be kept to a minimum if the limit is not to be exceeded.

Then too, the significance in this respect of the F_{25} components of various mean thicknesses is different. Those of similar mean to the resultant will have a minimum effect, while those varying widely in mean thickness from the resultant mean will have the greatest influence. This has been confirmed in Table XI for 10 per cent. of F_{25} components substituted in 60s, 64s and 70s and 10 per cent. of F_{20} components substituted in 60s, the 60s, 64s and 70s original being compounded of F_{15} components. As the substituted 10 per cent fraction changes in mean thickness from one side of the resultant mean to the other, there is a measurable change in the variability. This leads to a further conclusion—that a variable staple, whose mean is very different from the general stock mean has more influence on the variability than one whose mean is similar. In practice an F_{25} or F_{20} component whose mean lies beyond the fineness limits of 17-24 microns is more significant as a cause of variability than one lying within this range

In using an arithmetic treatment the actual examples of frequency distributions will be noted as being logarithmic normal rather than normal (Malan[11]), and the assumption has been made that the wools were reasonably sound as would be expected in worsted raw material, otherwise the upper limit to the coefficient of variation would have been above 30 per cent.

It is suggested that staples of over 20 per cent. coefficient of variation lying beyond the limits of 17-24 microns mean fineness are significant as increasers of variability, their significance being proportional to their quantity. It is also indicated that the higher the coefficient of variation over the 20 per cent. mark, the more significant in general the effect in increasing variability with respect to a limiting variability of 23 per cent for the resultant top. In general a stock is likely to have a coefficient of variation 3-5 per cent. above that of the average coefficient of its components The quantity of any coefficient of variation group and the actual variation, are interdependent in establishing the measure of the significance in increasing variability of the stock.

As a general guide to merino studbreeders, based on Noble combed top considerations alone, staples of coefficient over 25 per cent. should be regarded as undesirably variable, if present in any number, particularly if the remainder of the clip is of the order of 20 per cent coefficient of variation Odd cases in a uniform clip would be of negligible significance. As the average coefficient of variation of the staples in a clip approaches 20 per cent, then those of 21-25 per cent. coefficient become increasingly significant. In drawing these general conclusions, no attention has been given to genetic criteria, which may require lower limits if the topmaking raw material is to be kept within the suggested limits.

CONCLUSIONS

(1) In Australian woolsorting practice there may be wide limits in the crimp of the component staples in one quality number

(2) It is suggested that the value of the woolsorters' performance in reducing variability of the raw material may be over-estimated.

(3) If the large number of frequency distributions in each of the crimp groups is compounded into one frequency distribution for each group, the coefficient of variation of the resultant for the main groups is between 23-24 per cent. "Straight types" composed from a very wide range of sources would tend towards these values.

(4) For components of a limited range of variation, namely, 15-16 per cent, 20-21 per cent.; or over 25 per cent coefficient of variation, when compounded in proportions indicated by data concerning mean fineness distribution in the crimp groups and then further compounded in quality numbers, according to the proportions in which the crimp groups were represented in an authoritative assessment, the resultant coefficients of variation were several per cent higher than those of the components, namely.

	15—16%	20—21%	over 25%
60s	20·2%	24·2%	30·7%
64s	20·0%	23·9%	29·7%
70s	20·0%	23·4%	29·4%

(5) For a higher limit to coefficient of variation of fineness of 23 per cent. for merino Noble combed tops it is obvious that the average coefficient of variation of the components must be slightly below 20 per cent. and if components of over 20 per cent. are included, then a corresponding correction by the inclusion of components much less than the average is necessary, if the top variation is to remain within the upper limit.

(6) Components of over 25 per cent coefficient of variation in respect to fineness are particularly significant in causing the variability of an average "type" to increase rapidly

(7) The mean fineness of the variable components is also significant in increasing variability, as those whose mean is similar to the bulk cause less change than those which are more distant from this mean A merino component whose coefficient of variation is over 20 per cent. and whose mean lies outside the 17-24 micron range in regarded more significantly than those lying within. The significance is proportional to their quantity.

(8) The above conclusions are drawn on the assumption that 23 per cent is the upper limit to the coefficient of variation of mean fineness in practice in merino tops No attention has been paid to genetic criteria.

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REFERENCES

[1] Duerden, J E and Bosman, V *17th Rept Div Vet Services and Anim Ind. Union of South Africa*, 1931, 771-9
[2] Lang, W R *J. Text Inst*, 1947, 38, T241-256
[3] Barker, S G *Wool Quality* (H.M Stationery Office, 1931)
[4] Bosman, V *J Text Inst*, 1937, 28, P270-306, P321-353
[5] Stanbury, G. R *J Text Inst*, 1935, 25, P165-176
[6] Lang, W R. *J Text Inst*, 1947, 38, T257-270
[7] Daniels, H E. *Wool Industries Research Association Bulletin*, 1946, 10, 5, p 86
[8] du Plessis, A *The Marketing of Wool* (Pitman), 1930
[9] Bosman, V and van Wyk, C M *Onderstepoort Jnl Vet Sci and An Ind*, 1939, 13, 401-12
[10] Lang, W R *J Aus Inst of Agric Science*, 1946, 12, 108-110.
[11] Malan, A P. *Onderstepoort Jnl. Vet Sci. and An. Ind*, 1937, 9, 259-282

35—CALCULATION OF THE COEFFICIENT OF VARIATION OF FIBRE DIAMETER IN A BATCH OF SORTED WOOL BY SYNTHESIS OF VARIANCE

By R. C. PALMER

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In the foregoing paper Lang[1] has calculated the distribution of fibre diameter in a batch of sorted wool from a knowledge of certain data, which he has found experimentally.

His method of analysing the problem is consistent with the view that a wool sorter sorts by staple crimp He has accordingly found[2] the distribution of staple crimp in some typical batches of sorted wool, that is to say, he has found the frequency of occurrence, in the batch, of staples with six crimps per inch, seven crimps per inch, eight crimps per inch, *etc* Further, Lang[1] finds that the mean fibre diameter of staples of the same crimp class are not all the same, and he has measured[1] the distribution of staple mean fibre diameter within each crimp class. Finally the fibres in one staple have not, of course, all the same diameter, but have a certain spread about the staple mean.

There are thus three sources of variation of fibre diameter in the final sorted batch:

(*a*) Variation of crimps per inch from staple to staple, the sorter's contribution *i e. between crimp classes.*

(*b*) Variation of staple mean fibre diameter for the same crimps per inch, *i.e between staples within crimp classes.*

It will be convenient in what follows to call the mean fibre diameter within a staple the "staple diameter".

(*c*) Variation from fibre to fibre in the same staple, *i.e within staples*

To calculate the coefficient of variation of the final sorted batch, Lang[1] adds the various distributions together arithmetically. It is the purpose of the present note to show how the coefficient of variation of the sorted batch can be found quite simply from the three sources of variation above, by adding the squares of three coefficients of variation. The advantage of this method, apart from the saving of time, is that it shows clearly how the variability of diameter in the sorted batch arises, and enables one to see at a glance what would be the effect of altering one or other of the sources of variation.

SYNTHESIS OF VARIANCE METHOD AND DISCUSSION OF ITS ACCURACY

Make the approximation that all locks have the same total length, *i e.* that if all the fibres are put end to end, the length of this line is the same for each lock This approximation is also inherent in the arithmetical summation method

Variation of Staple Diameter

The coefficient of variation of staple diameter is almost constant from crimp class to crimp class This can be seen from Table I, which shows these coefficients of variation calculated from the data given by Lang.[1] The coefficient of variation shows no trend with crimp class and so we may probably safely ascribe the variations to random sampling. Whatever the cause of the variations, however, it is evident that they are small and that it is consequently a good approximation to take the coefficient of variation as constant. It is this fact that makes easy the short method of calculating the coefficient of variation of the sorted batch For, if the coefficient of variation is constant from crimp class to crimp class, the standard deviation of log (staple diameter) will be constant from crimp class to crimp class, since the standard deviation of the log distribution is equal to the coefficient of variation (expressed as a fraction not as a percentage) of the corresponding ordinary distribution. This is strictly only an approximation, but is a good approximation if the coefficient of variation is small and the distribution is fairly symmetrical, both of which conditions are satisfied in this case.

Table I

Mean and Coefficient of Variation of Staple Diameter* within various Crimp Classes

Crimps per inch	Staple diameter*		Degrees of Freedom on which Coefficient of Variation is based
	Mean, μ	Coefficient of Variation	
4	26·5	18·4	7
5	25·7	12·3	38
6	24·2	12·0	159
7	22·9	11·0	165
8	21·9	13·6	363
9	21·4	11·7	217
10	20·5	13·3	477
11	20·4	12·8	185
12	19·6	12·9	315
13	19·4	12·0	89
14	19·8	13·2	130
15	19·5	13·4	47
16	18·6	14·0	113
17	19·5	13·0	12
18	18·4	10·8	18
19	17·2	12·1	13
20	16·5	15·6	21
21	20·0	14·2	1
22	16·1	9·4	11
23	15·0	18·9	5
24	14·6	5·6	6
Average		12·8	

* By "staple diameter" is meant the mean fibre diameter within a particular staple.

Variation within a Staple

If the coefficient of variation of fibre diameter within a staple is taken as constant from staple to staple, the same remark applies, *viz.* that the standard deviation of log(fibre diameter) will be constant from staple to staple. In this case the highest coefficient of variation considered by Lang,[1] 0·28 (28 per cent.), is on the border line of "small"; but the approximation is still fairly good as will be seen later.

Since on the one hand the coefficient of variation of mean diameter from staple to staple within a crimp class, and on the other hand the coefficient of variation of individual diameter within a staple are both constant, we can find the coefficient of variation of fibre diameter *within a crimp class* by adding the squares of the two first mentioned coefficients of variation. This process is equivalent to adding variances of the corresponding logarithmic distributions. In other words when in a set the distributions are log normal, in place of the well known additivity of variances it is convenient to use the additivity of coefficients-of-variation-squared.

Of the three sources of variation, (*a*), (*b*) and (*c*), listed above, two, *viz* (*b*) and (*c*) are thus readily found. For the item (*c*) we take the arbitrarily chosen within staple coefficient of variation, for example 15·5 per cent. or

20·5 per cent. as chosen by Lang For item (*b*) we take the average coefficient of variation between staples within a crimp class, which for merino wool is 12 8 per cent (see Table I). Item (*a*) is found as in the next paragraph.

Variation between Crimp Classes

The "between crimp classes" contribution is found by calculating the coefficient of variation of mean staple diameter between crimp classes. Take as an example the distribution of crimp classes in the 64s wool sorted by the Melbourne group of assessors (Lang[1]) given in Table II. In this wool the crimp classes shown in the first column occurred with the frequency shown in the second column. Now the average staple diameter for staples of 8 and 9 crimps per inch is 21 73 μ, and so on (see Table II).

Table II

Crimps per inch	Frequency	Mean diameter, μ
8— 9	0 075	21·73
10—11	0·425	20 46
12—13	0 350	19 60
14—15	0 075	19·70
16—17	0·075	18·68

The second and third columns of Table II form a little diameter distribution whose coefficient of variation is found to be 3 5 per cent

The Addition of the Variances

It is now possible to find the coefficient of variation in a sorted batch composed of staples of any chosen within staple coefficient of variation We have

(*a*) between crimp classes coefficient of variation = 3 5 per cent.

(*b*) between staples within crimp classes coefficient of variation = 12·8 per cent.

(*c*) within staple coefficient of variation (as under).

This leads to the results given in Table III. Note that it is not necessary for calculation purposes to express the coefficients of variation as fractions; they can be used directly as percentage figures, when the final result will also be given as a percentage.

Table III

Within staple Coefficient of Variation	15 5%		20 5%		27 6%	
	Coefficient of variation	(Coefficient of variation)^2	Coefficient of variation	(Coefficient of variation)^2	Coefficient of variation	(Coefficient of variation)^2
Between crimps	3 5	12	3 5	12	3 5	12
Between locks	12 8	164	12·8	164	12 8	164
Within locks .	15·5	240	20 5	420	27 6	762
Total		416		596		938
√=resultant Coefficient of Variation		20 4		24 4		30·6
Value obtained by arithmetical summation ...		20 0		23 9		29·7

27 6% was chosen because it is the average C of V within staples for those staples whose within staple coefficients of variation are over 25% as found by Lang.

The results by synthesis of variance and by arithmetical summation are not identical because (i) writing the square of the coefficient of variation for the variance of the log distribution is only an approximation, (ii) in the arithmetical summation method individual between-lock-within-crimp class distributions are used whereas we have used the mean coefficient of variation of them all, 12·8 per cent. If the reason for the variation of the coefficients of variation in Table I is really just random sampling variations, as seems likely, then to take the mean coefficient of variation, 12·8 per cent., is better than to take the individual distributions, and to that extent this short method is better than the summation method. But the chief cause of the small discrepancy between the two sets of results is probably reason (i). We conclude then that the values given by the short method are likely to be in error by a maximum of about one unit in coefficient of variation. This error, however, is unimportant because the values deduced by the short method will form a consistent set, that is to say comparisons can be made amongst them with confidence.

The chief advantage of this method over arithmetical summation of distributions is that it displays the sources of variation and their contribution to the variation in the final sorted batch. The whole process resembles an analysis of variance in reverse, in fact it is a synthesis of variance.

MORE COMPLICATED CASES

1. Within Staple Coefficients of Variation not all the same

Where the staples do not all have the same within staple coefficient of variation, one must of course use a weighted average for the within staple coefficient of variation. Consider as an example a batch of similarly sorted 64s wool, composed of seven parts of staples having a 15·5 per cent. coefficient of variation, two parts of staples having a 20·5 per cent. coefficient of variation, and one part of staples having a 27·6 per cent. coefficient of variation. This is one of the examples considered by Lang. The addition of coefficients-of-variation-squared is carried out thus:

Between crimp classes	$(3{\cdot}5^2)$		12
Between staples within crimp classes	$(12{\cdot}8^2)$		164
Within staples	$(0{\cdot}7\times15{\cdot}5^2)$	168	
	$(0{\cdot}2\times20{\cdot}5^2)$	84	
	$(0{\cdot}1\times27{\cdot}6^2)$	76	
			328
			504

square root=coefficient of variation of sorted batch=22·5%.
Result obtained by arithmetical summation, 22·7%.

2. The Coefficient of Variation of a Mixture of two or more Batches

Suppose that one mixes two batches of wool, each with its own mean diameter and coefficient of variation, what is the coefficient of variation of fibre diameter in the mixture? Let the two components be mixed as follows:

fraction x_1 of component 1 with mean diam. d_1 and coefficient of variation C_1
,, x_2 ,, ,, 2 ,, ,, ,, d_2 ,, ,, ,, ,, C_2

Then it can easily be shown that the resultant coefficient of variation is given by

$$C^2=x_1C_1^2+x_2C_2^2+10{,}000x_1x_2\times2{\cdot}30^2\times\left(\log_{10}\frac{d_1}{d_2}\right)^2$$

(If the coefficients of variation are expressed as fractions, not as per cent., the factor 10,000 is left out.) From this formula it follows at once that C_1 and C_2 are fixed, and if x_1 and x_2 are fixed, then C is a minimum when $d_1=d_2$.

That is to say if two batches of wool each with a given coefficient of variation are mixed in a given ratio, the coefficient of variation of the mixture will be a minimum if the two batches have the same mean fibre diameter. This is one of the conclusions derived from the arithmetical summation method.

To investigate the accuracy of the above formula consider the addition of one part of a stock of 27·6 per cent. coefficient of variation and various mean diameters to ten parts of a stock of mean diameter 20·7μ and coefficient of variation 20·0 per cent. These syntheses of variance are given in Table IV.

Table IV

Synthesis of Variance for the Addition of 10% of Components of over 25% Coefficient of Variation to a Stock of mean Diam. 20·7 μ and Coefficient of Variation 20·0%

Source of variation	Diameter of addition, μ						
	15	17	19	21	23	25	27
X .	360	360	360	360	360	360	360
Y ..	76	76	76	76	76	76	76
Z	93	35	7	0	10	36	64
Total ...	529	471	443	436	446	472	500
Resultant Coefficient of Variation ..	23·0	21·7	21·0	20·9	21·1	21·7	22·4
Value obtained by arithmetical summation .. .	21·8	21·4	20·6	20·3	21·3	21·9	22·7

X=Contribution of original stock, $x_1\ C_1^2$
Y=Contribution of added stock, $x_2\ C_2^2$
Z=Contribution due to difference in means $10{,}000 x_1\, x_2 \times 2{\cdot}30^2 \times \left(\log_{10}\frac{d_1}{d_2}\right)^2$

This example is unfavourable to the formula because the approximation that the standard deviation of a distribution of logarithms is equal to the coefficient of variation of the corresponding ordinary distribution holds only for small coefficient of variation, and 0·276 is on the borderland of "small" Yet the values obtained by the formula agree quite well with the arithmetically derived values. The only exception is the first result (23·0 as against 21·8), and in this case the arithmetical value is probably partly in error due to the random sampling errors inherent in using an actual sampled distribution, as one must in the arithmetical method.

The formula can easily be extended to cover a mixture of three or more batches all with different means and coefficients of variation. If fractions, $x_1 x_2 x_3$ of batches of wool of mean diameters $d_1\, d_2\, d_3$ and coefficients of variation $C_1 C_2 C_3$ are mixed, the coefficient of variation of the mixture C is given by

$$C^2 = x_1 C_1^2 + x_2 C_2^2 + x_3 C_3^2$$
$$+ 10{,}000 \times 2{\cdot}30^2 \left\{ x_1 x_2 \left(\log_{10}\frac{d_1}{d_2}\right)^2 + x_2 x_3 \left(\log_{10}\frac{d_2}{d_3}\right)^2 + x_3 x_1 \left(\log_{10}\frac{d_3}{d_1}\right)^2 \right\}$$

AN APPLICATION

Lang[1] gives two examples of sorted wool which in his experience are extremes. These are given in Table V Both are 64s quality. In A staple crimps only vary from 8 crimps per inch to 15, while in B the variation is from 6 to 20 crimps per inch The mean staple diameter corresponding to each crimp class is taken from Table I. The two distributions in Table V are considered as diameter distributions, and the means and coefficients of variation are given at the bottom of the Table Let us take the within staple coefficient of variation as 20 per cent. The between staple-within-crimp-class coefficient of variation is 12·8 per cent. (see Table I) The syntheses of variance for the two wools A and B are then as in Table VI.

Table V. Distribution of Crimp Classes in two Batches of sorted 64s Wool

Crimps per inch	Mean staple diameter, μ	Frequency Wool A	Frequency Wool B
6	24·2		4
7	22·9		2
8	21·9	3	6
9	21·9	8	6
10	20·5	19	10
11	20·4	26	10
12	19·6	19	14
13	19·4	16	10
14	19·8	6	12
15	19·5	3	7
16	18·6		7
17	19·5		2
18	18·4		6
19	17·2		2
20	16·5		2
Mean diameter		20·2	20·0
Coefficient of variation, %		3·7	7·2

Table VI. Synthesis of Variance for the two sorted Wools of Table V

	Wool A		Wool B	
	Coefficient of variation	(Coefficient of variation)^2	Coefficient of variation	(Coefficient of variation)^2
Between crimp classes	3·7	14	7·2	52
Between staples within a crimp class	12·8	164	12·8	164
Within staples .	20	400	20	400
Total		578		616
Resultant Coefficient of Variation		24·0		24·8

There is very little difference between the resultant coefficients of variation 24·0 and 24·8. This is because as can be seen from the Table the "Between crimp class" contribution (14 and 52 respectively) is quite a small part of the total Wool B, with its large range of crimping and so of staple diameter, would normally perhaps be considered badly sorted, yet the variability of diameter in this sorted batch is very little worse than that of the carefully sorted wool A

Even a batch of wool sorted from these same fleeces staple by staple so as to contain only staples of a single crimp class, say 11 crimps to the inch, would have a coefficient of variation $\sqrt{(0+164+400)}=23·8$ per cent , hardly different from that of wool A, 24·0 per cent. If a wool sorter judges by crimp alone, therefore he can cut down variability in his raw material only to a very limited degree

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REFERENCES

[1] Lang, W. R *J Text Inst*, 1949, 40,
[2] Lang, W R *J Text Inst*, 1947, 38, T257
[3] Lang, W R. *J Text Inst*, 1947, 38, 1241

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36—AN ELECTRON MICROSCOPIC EXAMINATION OF WOOL CONTAINING POLYMER

By E. H. MERCER*

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INTRODUCTION

Speakman and Lipson[1,2] have shown that the properties of wool may be usefully modified by the deposition of polymers within them. Little evidence of the polymer present in quantities up to 30 per cent. can be found by means of the optical microscope. When the polymer content is high, small amounts may be seen on the surface of the fibres but the greater amount is within.[2] By the adoption of special techniques a certain amount of the internally deposited material can be located by means of the electron microscope. The methods employed and the subsidiary experiments necessary for the interpretation of the results are described below.

In instances where the electron microscope has been used to examine fibres it has been necessary to overcome the difficulty raised by the excessive thickness of the material by resorting to surface replica techniques or by breaking the material into small enough fragments. A wool containing a melamine polymer has been previously examined after mechanical grinding,[3] but this method of preparation yielded irregular fragments from which it was difficult to deduce anything. A preferable method of breaking wool down is that of enzymic digestion,[4] and the appearance in the electron microscope of wool fragments obtained in this way has been made familiar by many studies.[5,6,7] The method is not always applicable because some polymers, either by reason of their forming an impervious surface layer or by a reaction with the protein of the fibre, may make the fibres resistant to digestion. This proved to be the case with fibres containing polymethylmethacrylate, which on other grounds is known to form a surface coating. A wool containing polymethacrylic acid was found to be readily digested by trypsin and forms the subject of this investigation.

EXPERIMENTAL

(a) *Deposition of the polymer*

A Southdown wool was impregnated with the polymer by Dr. M. Lipson of this department using the method described by Lipson and Speakman.[1,2] The polymer content was 23 per cent.

(b) *Tryptic digestion and optical microscopy.*

The sample was retted in a 0.05 per cent. solution of commercial trypsin at *pH* 8.6 and 40° C. At the end of three weeks the fibres were extensively attacked. A sample of the same wool serving as a control was somewhat less attacked. The component cells, cortical and cuticle, of the fibres were released by shaking the retted wool with glass beads. Plates 1 and 2 are comparable optical micrographs of original retted wool and of the wool which contained polymer. The long thin cortical cells predominate in each preparation but in the sample containing the polymer many additional fine particles are to be seen in the field. Most of these are fragments of cells but some particles of polymer may be present. Since the poly acid confers on the wool an enhanced affinity for basic dyes the reaction with such dyes may be used to distinguish the two preparations. From the retted and partially disintegrated fibres containing the polymer some interesting optical micrographs which illustrate clearly some features of the structure of the fibre were obtained after staining The cuticle cells picked out by absorption of the dye may be seen partly separated from the fibre as in Plate 3. The cell suspension such as that illustrated in Plate 2 is stable at *pH* above 8 for some days If the *pH* was lowered to 3 (approximately) the suspension flocculated at once. This seems to indicate that the suspended particles are covered with polymer and this layer determines their behaviour in suspension.

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(*c*) *Electron micrographs.*

The microscope used was an R C A. Type B located at the Shirley Institute, Didsbury

The cell suspension was dialysed to remove salts until the *pH* approached 7 This solution was slimy to the touch, slow to settle and acidification produced immediate flocculation Electron micrographs were taken of both the suspended and flocculated material. In each case the material was gently ground in the wet state and a drop of the suspension dried on the conventional collodion grid. Electron micrographs of the acid flocculate and dialysed suspension are shown in Plates 4 and 5, respectively. The preparation after flocculation obviously contains two kinds of material, marked W and P in Plate 4. W is easily recognised from its fibrous character as fragments of cortical cell from the wool Comparison may be made with the plates of similar material derived from retted wool reproduced by Mercer and Rees.[7] *e.g* Plate 7. The component P yields fine stringy formations with a tendency to be drawn out into threads and is easily distinguished from the keratin fibrils It is present in the original digest in colloidal solution and on drying yields continuous films. If Plate 5 is examined the fibrils of wool may be seen obscured by the thick film which covers the whole preparation. These observations point to P being polymer Evidently the strongly acid polymer is soluble or is finely suspended in alkaline solution and dries to a coherent film In acidified solutions it separates out to form a discrete component.

(*d*) *Further identification of the polymer by means of X-Rays.*

Although the appearance of the component P in the electron micrographs is consistent with its being polymer, further confirmation was sought by means of X-rays A small amount of this component was separated for analysis as follows. The retted suspension was rendered more alkaline by the addition of ammonia (*pH* 9) and macerated to induce the polymer to separate from the wool. The cells were allowed to separate out from solution and the permanent suspension acidified. The white flocculent was filtered off, washed by water, dried and X-rayed. The resulting pattern was compared with that obtained from polymethylmethacrylate polymerised in vitro. The pattern given by the polymer is a typical amorphous-photograph consisting of two diffuse rings indicating commonly occurring spacings of 5·4 and 2·8 A.[8] The extracts from the wool, of which the electron micrograph, Plate 6, is typical, gave the same two diffuse rings and two other faint rings at 10 and 4-5 A, which are attributed to traces of protein. In the absence of other possibilities the similarity of the patterns is sufficient to identify positively the polymer.

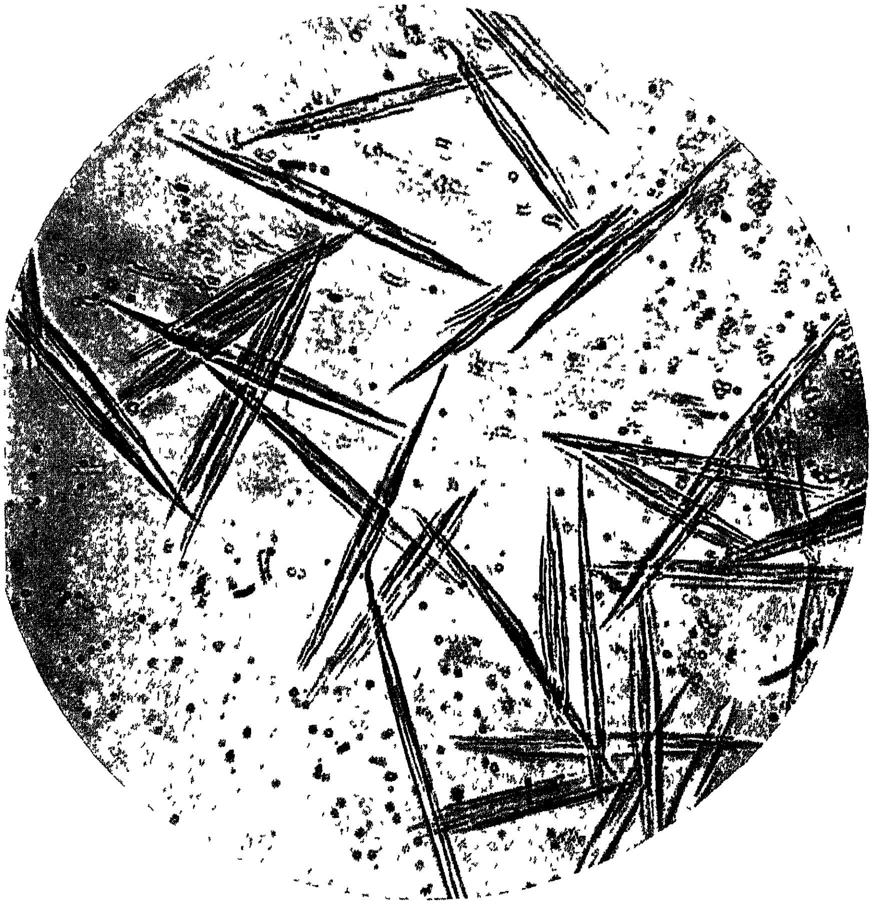

Plate 1

Cortical cells from original wool Optical micrograph The cells are about 100μ long × 400

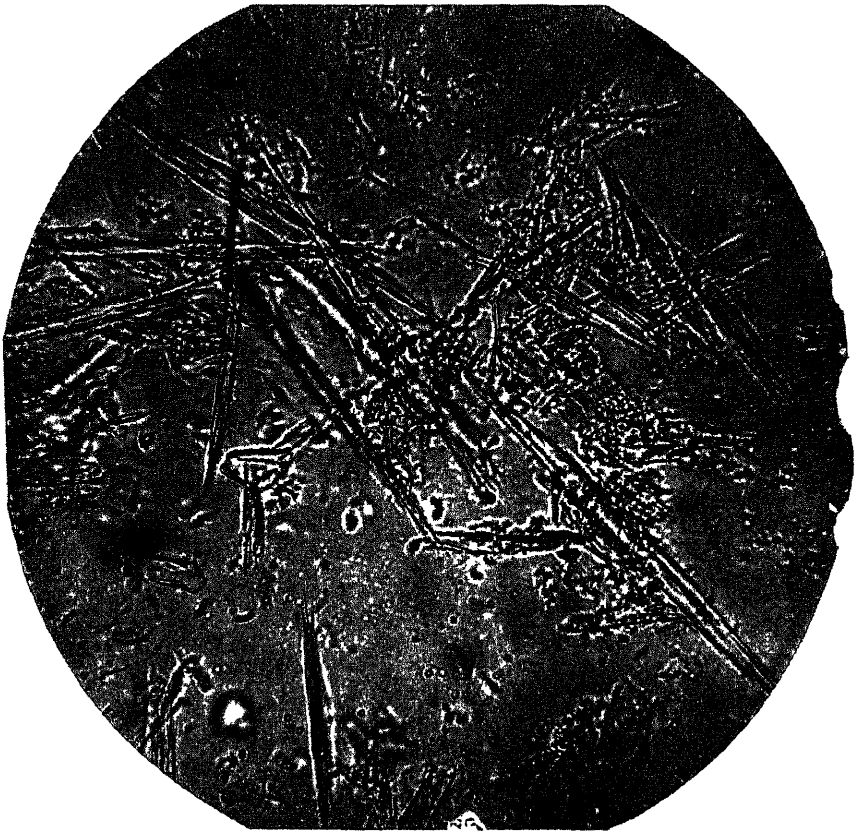

Plate 2
Cortical cells and debris from wool containing polymer, after retting
× 400

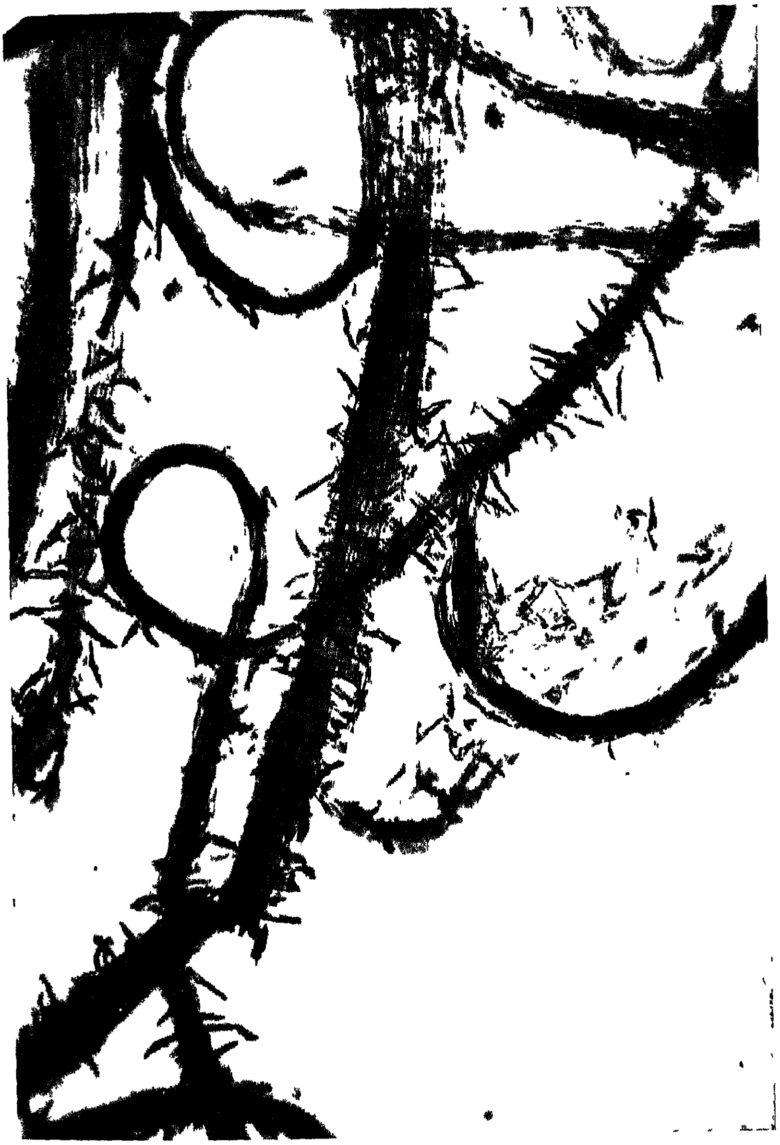

Plate 3
Partly retted wool containing polymer and stained with methylene blue The separation into cuticle cells (scales) and cortical cells is clearly visible × 650

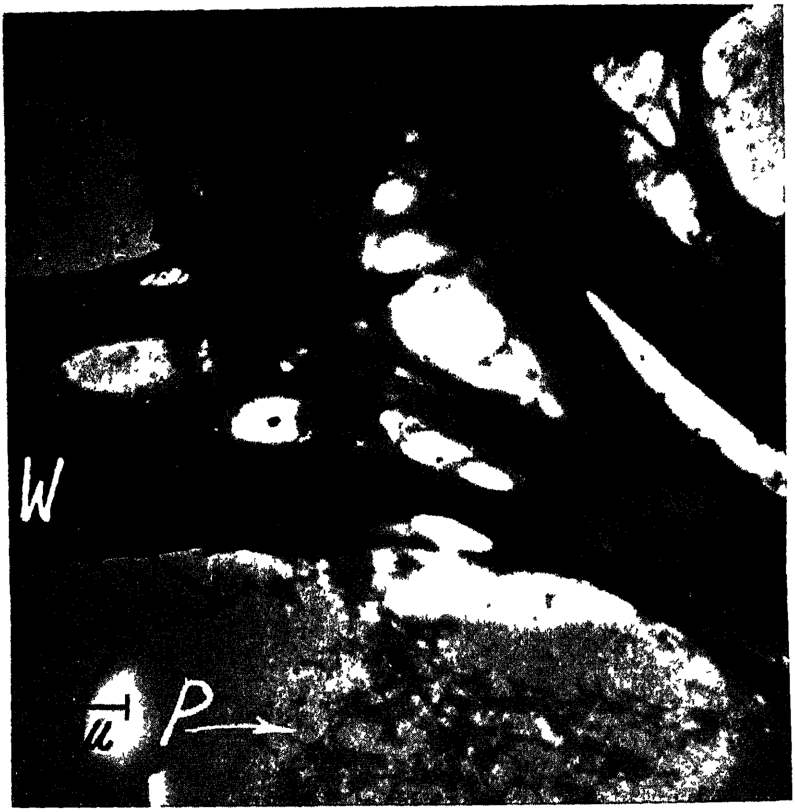

Plate 4
Electron micrograph of the acidified suspension of retted material obtained by retting polymer-containing wool × 10,000

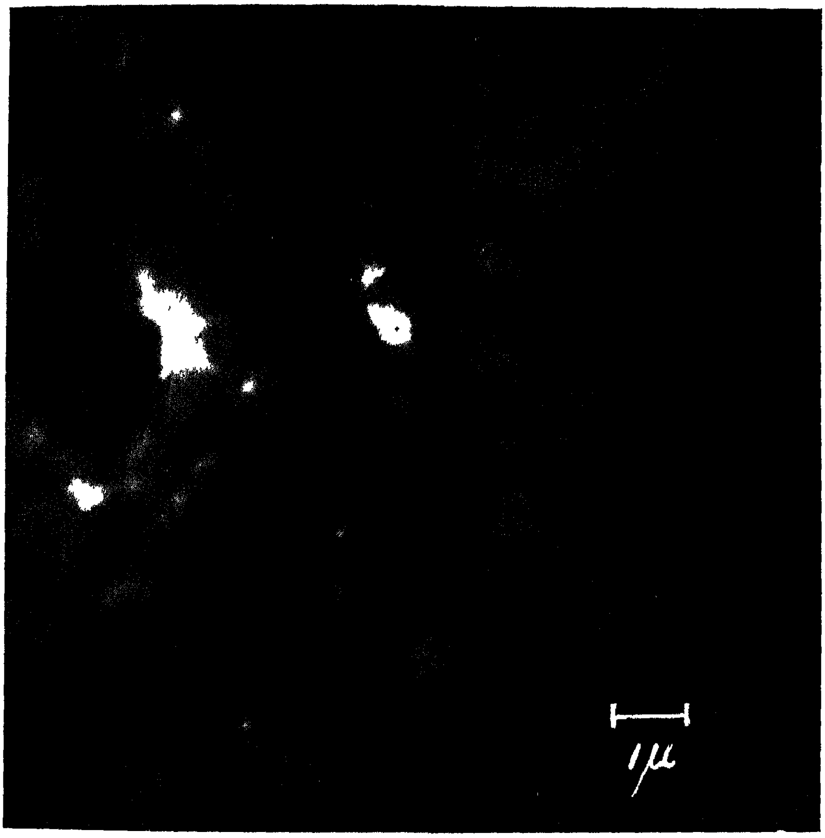

Plate 5

Electron micrograph of the suspension of tryptic digest from wool containing polymer The polymer largely in colloidal solution has formed a film obscuring the details × 10,000

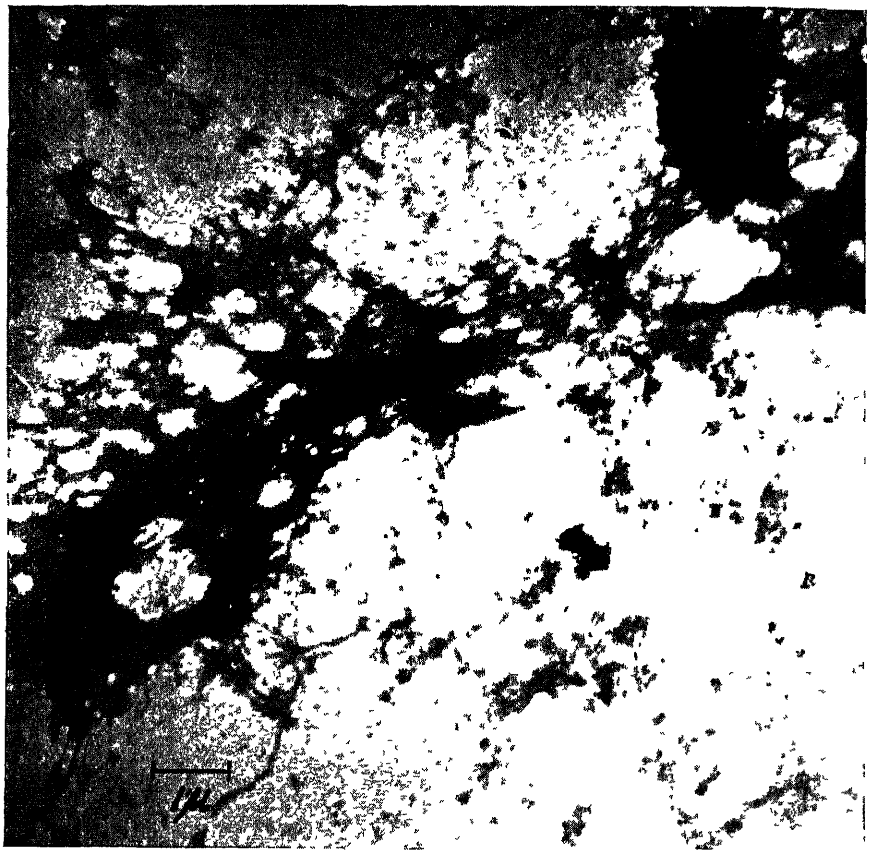

Plate VI
Polymer particle from retted wool Material used for X-Ray examination
× 10,000

Plate 7
Fibrillae from cortical cell without polymer (Mercer and Rees (7))

DISCUSSION

The main objects of this examination were to detect the presence of polymer and locate the site of deposition within the fibres The component present in the original digest as a colloidal suspension and in the acidified digest as a discrete precipitate easily distinguished from the fibrils of wool, has been identified as the polymer. It is present as a substantial fraction of the total material in micrographs such as Plate 4 A considerable amount of the polymer is therefore present in those parts of the fibre external to the main non-digestible fibrillar phase (Figure 1f), *i e* it is present in pore spaces or in the inter-fibrillar and inter-cellular phase (amorphous matrix) of the fibre shown black in Figure 1 It is not possible to conclude from the electron micrographs anything concerning the actual condition of the polymer in the original wool because neither the tryptic digest nor the acidified material of Plates 4 and 6 represents the polymer in an original condition However since polymethacrylic acid prepared in vitro does not dissolve in buffers at *pH* 8 6 such as was used for digestion, it is a fair conclusion that the polymer in colloidal suspension in the tryptic digest entered solution as the wool dissolved because it was so finely divided The same conclusion, that the polymer is present in the fibre in a finely dispersed form, might also be deduced from the very diffuse X-ray patterns obtained from wool containing the polymer [8]

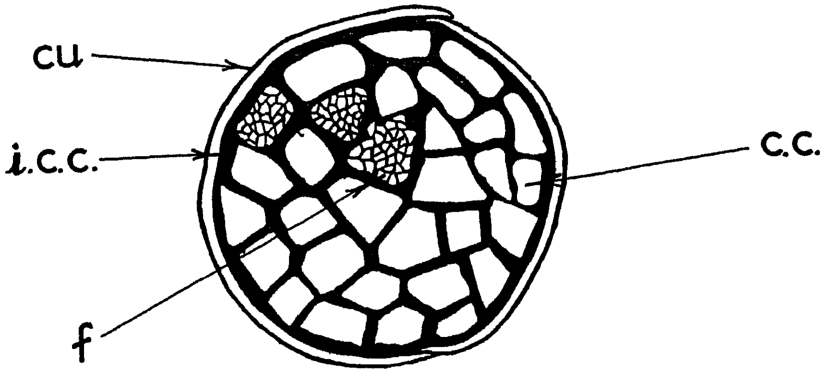

Fig 1

Cross-section of a non-medullated wool fibre showing scale cells of cuticle *cu*, cortical cells *c c*, intercellular cement *i c c* Each cell is a bundle of fibrils *f*, and between fibrils there is a small amount of cementing substance or matrix The fibrils have been shown in a few only of the cells The polymer is deposited mainly in the regions shown black between the cells and fibrils

Lipson found that fibres containing polymer were harder to stretch in water of neutral *pH* and Onions has noted that the normal onset of the α-β transformation is delayed on stretching in water.[8] Extension is easier and the course of the α-β transformation is more nearly normal in alkaline solutions (*pH* 11). These observations may be explained if we consider that in the initial stages of stretching (0-20 per cent) the extra-fibrillar phase is responsible for the greater part of the observed extension,[9] and that in this phase we are stretching both polymer and keratin In acid and neutral solutions the acid polymer is in a condensed and coherent condition resistant to extension, so that the work of extension is high The polymer also appears to prevent the entry of water into the crystalline phase so that on extension the transformation of the α-crystallites into the β-form is delayed as is the case with dry fibres. In alkaline solutions the acid groups of the polymer network ionise permitting swelling and easy unfolding of polymer and protein.

From the electron micrographs no conclusions can be drawn as to the presence or absence of polymer in small quantities in the fibrillar phase of the fibre, nor is it possible to detect whether a portion of the polymer has entered into chemical association with the protein to form actual chemical links within the protein network.

SUMMARY

An electron microscopic examination of material obtained by the tryptic digestion of wool containing polymethacrylic acid shows the presence of both typically fibrous cortical cells of wool and also of the polymer. Optical and electron optical micrographs of the retted wool are shown. The polymer seems to be deposited during polymerisation chiefly in the extra-fibrillar regions (pores and matrix) of the fibres Since these regions are stretched first the fibres are harder to stretch in acid and neutral solutions when the polymer is in a condensed and coherent form. In alkaline solutions the acid polymer ionises and the complex is more easily extensible.

ACKNOWLEDGEMENTS

The author wishes to thank Dr M. Lipson for the preparation of the polymer containing wool, Mr W. J Onions for permission to quote his unpublished X-ray observations, the Director of the Shirley Institute for permission to reproduce the electron micrographs, and Dr D G Drummond of the Shirley Institute for help in the use of the microscope

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REFERENCES

[1] Speakman and Lipson, *Nature*, 1946, 157, 736
[2] Lipson Ph D. Thesis, Leeds, 1948
[3] Powers *Industrial and Engineering Chemistry*, February, 1945, 188.
[4] Burgess *J Text Inst*, 1934, 24, T 289
[5] Zahn *Mell Textilber*, 1940, 21, 505.
[6] Hock and McMurdie *J Res Nat Bur Stand*, 1943, 31, 229.
[7] Mercer and Rees *Aust J Exp Biol*, 1946, 24, 175.
[8] Onions Unpublished observations
[9] Astbury and Woods. *Phil Trans Roy Soc*, 1933, *A* 232, 333.

37—THE FORMATION OF KERATIN DURING HAIR GROWTH

By E H. Mercer*

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INTRODUCTION

Artificial fibres are produced from suitable synthetic or natural polymers by the familiar processes of extrusion and drawing Among the natural fibres silk appears to be formed in an analogous way, and it has been suggested that possibly the animal fibres, hair and wool, are also extrusions from the hair follicles of the skin [1] An examination of the histology of the hair root shows, however, that, even if extrusion plays a part, the process is a good deal more complex Unlike silk threads animal hairs are cellular structures consisting of three regions, cuticle, cortex and medulla, composed of very different kinds of cells Of these the long thin cells of the cortex are the basis of the elastic properties of the fibres[2,3] and it is therefore their formation that is of the greatest interest.

Each individual hair originates in a single follicle and the detailed histology of the process has been studied very extensively.[4] In a longitudinal section of a straight hair root the history of the presumptive cortical cells may be followed easily. As indicated in the diagram Figure 1, they arise as rounded close-packed bodies in the vicinity of the papilla at the base of the root. On moving away from the papilla along the shaft of the follicle they elongate, become fibrous in appearance, and finally harden to produce the "spindle-shaped" resistant forms which can be isolated from the final fibre Although the principal features of histology of the developmental process are well understood, the sequence of events at the molecular level within the cells, *i e.* the synthesis of the fibrous protein itself, which accompanies the visible changes and finally results in the conversion of the cells into solid oriented keratin, is still obscure Much is known, however, of the molecular structure of the keratin of the final cortical cells owing largely to the work of Astbury and his collaborators [5,6] The long chains of the protein appear to be extended in the direction of the fibre axis, *i e.* the long axis of the cortical cells, and to be cast into more or less regular folds This small scale molecular regularity gives rise to what is referred to as the large angle X-ray pattern, in this case the α-pattern, when a photograph is made by directing an X-ray beam at right angles to the fibre axis The same large angle patterns are also given by several other proteins showing that these, too, have the same basic molecular framework as hair keratin and enabling a class of proteins to be defined on the basis of their X-ray patterns [6]

In addition to the small scale regularities there occur larger regularities (long-spacings) in many protein fibres, including hair, which may be detected by X-rays (small angle scattering) or by electron microscopy. The nature of these regularities is not fully understood, but there is no doubt that many protein fibres consist of a very complicated system of "patterns within patterns" It is plausible to see the origin of these patterns in the peculiarities of the synthetic process by which they are brought into being and to expect that studies of molecular and histological development will assist each other

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The traditional histological techniques, however, are not designed to cast light directly on problems of molecular structure unless the structural features themselves happen to be associated with some specifically stainable complex. This not always the case, for as has been mentioned above, structural frameworks may be common to whole classes of proteins, whereas the staining properties are mainly dependent on the chemical character of the associated side chains of secondary importance in the structure sense.

Those properties in which we are interested here, the nature of the basic pattern, the level at which it appears, its type, perfection and orientation, and the stability of these features towards chemical and physical change, have therefore to be specially studied by such methods as X-ray diffraction, birefringence measurements and special histochemical techniques.

We know from the important histochemical studies of Giroud and Bulliard[7] that in the development of all keratinised tissues, skin, hair, nails, *etc.*, the softer tissues which underlie the hardened parts react vividly to the nitroprusside test for thiol groups (SH), and that as the tissues harden, the reaction fades. Chemical observations on wool and hair have related the chemical inertness and the physical toughness of the keratins as a class to the large proportion of cystine bridges made possible by the high cystine content.[8,9] It is obvious, therefore, that the unconsolidated precursor of keratin proper is a reduced form of the protein in which some of the disulphide bridges have yet to be formed This protein may be called a "pre-keratin".* One of the reactions associated with hardening is then the oxidative closure of the thiol groups to form disulphide bridges:

$$\mathrm{P-SH+HS-P \rightarrow P-S-S-P}$$

(P=peptide chains of protein)

Marston stated that copper in some form is necessary to catalyse this reaction for in its absence the hardening is slow and incomplete.[10] Rudall has isolated what is probably the pre-keratin of skin or a related protein by extracting the germinal layers with strong urea [11] The protein dissolves and can be precipitated from urea solution by the addition of salt solutions and then formed into fibres X-ray examination of these fibres showed that the protein was in the α-form At this stage in the development the protein therefore already possesses the same basic framework as the final keratin but lacks those crosslinks which render it insoluble in urea It is possible to reverse this final step in the process and to obtain from wool and hair a protein derivative in most respects similar to Rudall's protein by reduction followed by extraction with urea solution This extracted protein may also be formed into fibres, which give the typical α-X-ray pattern [12]

THE HAIR FOLLICLE AS AN EXPERIMENTAL MATERIAL

The further investigation of these problems to be described below has been made using the single hair root as a research material. This was made possible by the fact that a plentiful supply of hair roots may be obtained by plucking from the human head When suitably mounted, the histological structures of interest are easily visible in such plucked roots and the several stages in the developmental process are conveniently set out in order along the follicular length. The act of plucking does not produce serious distortion as can be seen by comparing plucked roots with those sectioned *in situ* Although the greater part of the work was carried out on human material, the findings have been confirmed on roots obtained from cow skin and sheep.

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* The term "pre-keratin" employed here refers to Giroud and Bulliard's usage and not to the more restricted pre-keratinisation zone of some other workers.

The presumptive cortex, the root sheaths and the fibre itself are all birefringent or doubly refracting and are most easily distinguished if a polarising microscope is used.[13] The amount of the double refraction (DR) is of value as an indication of the occurrence of oriented structures and has been of great use in the present study. For the measurement of the degree of DR a Sénarmont compensator was mounted on a microscope to measure

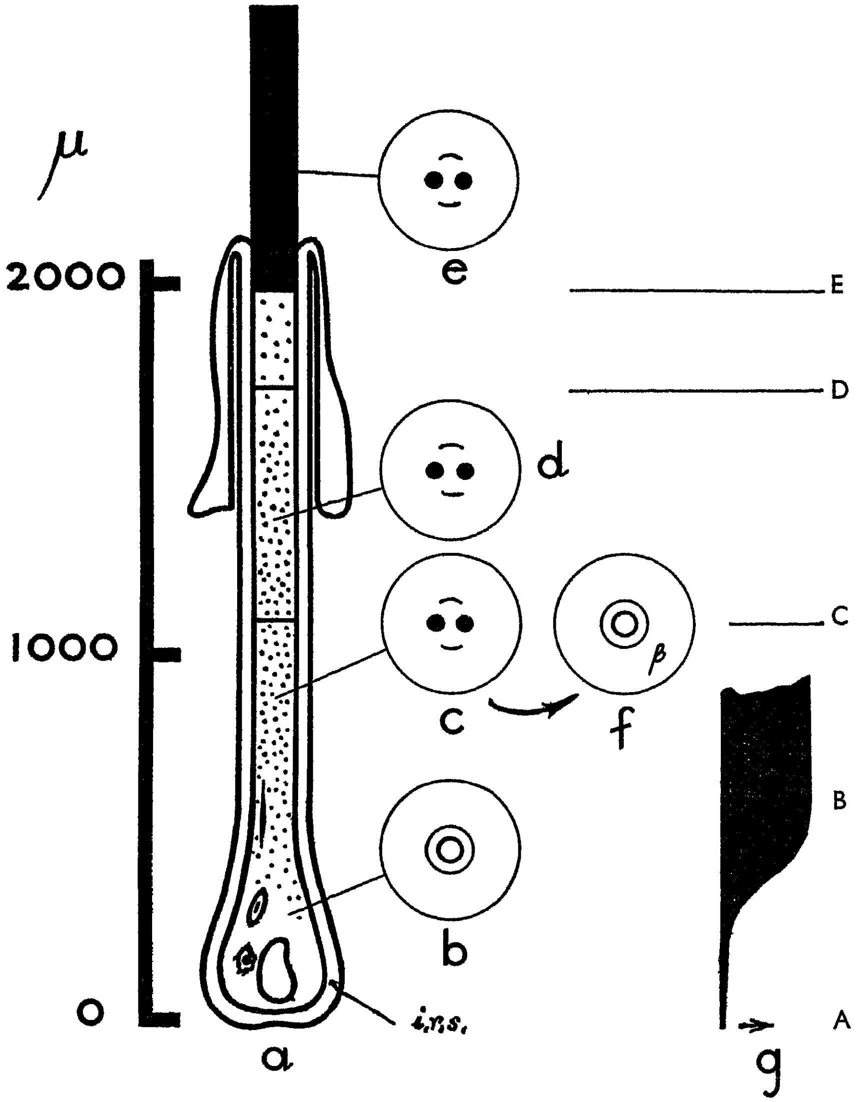

Fig 1

Some features of the development of the presumptive cortex of the follicle from the human head (*a*) is a longitudinal section of a plucked hair root The inner root sheath (i r s) and the precortical regions are shown The pre-keratinous region (positive thiol reaction) is dotted (*b*), (*c*), (*d*), (*e*) and (*f*) are the type of X-ray patterns obtained from the levels shown (See text) At (*g*) the development of birefringence (DR) is shown in relation to the distance along the follicle Note the rapid rise at the level B.

the total phase difference and a micrometer eye-piece was used to obtain the thickness of the fibre. The DR per unit thickness of the material was then calculated thus:

$$n_2 - n_1 = \frac{\delta\lambda}{t}, \text{ where} \begin{cases} \delta = \text{phase difference} \\ \lambda = \text{wavelength} \\ t = \text{thickness.} \end{cases}$$

A hair root is plucked and mounted in an inert mountant and examined at once. It is necessary in many of the experiments to use freshly obtained specimens. When the DR is measured at many points along the follicular length a curve similar to that shown on the right of Figure 1 at (*g*) is obtained showing the way in which the oriented properties of the hair appear. It will be seen that the bulb region is almost isotropic, and that at the level of the constriction of the root the DR rises suddenly[13] to the full value of the final fibre.

This same conclusion was reached also by taking X-ray micrographs of the bulb at A and of the pre-cortex immediately above B. A single follicle hardened in formalin was used in this exacting work, which necessitated the use of a fine 0·01 cm collimator and a long exposure time of the order of 24 hours at a specimen-to-plate distance of one cm. Filtered radition from a copper anode filament tube run at 20 m.a. was employed. The pattern from the bulb consisted of two diffuse rings similar to the type of pattern usually yielded by poorly organised organic material indicating only the presence of unoriented native protein. At all levels above B a well oriented α-type pattern, similar to that of the final wool, resulted These patterns and the levels at which they were obtained are set out in the centre of Figure 1 Both methods agree in showing that in the molecular sense a fibrous structure typical of the final hair forms low down in the follicle at the level of the constriction, which is therefore called the fibrillation zone. In the optical microscope fibrils are to be seen first at this same level [7] The pre-keratinous zone, discovered by Giroud and Bulliard,[7] characterised by the presence of free thiol groups, extends from the level B to E, a distance in the human follicle of about 1700μ The α-keratin structure is thus established at the beginning of the pre-keratin and all subsequent reactions and modifications serve only to consolidate it without producing any substantial changes in either DR or X-ray pattern

At the level of the contraction of the root there thus occur changes which produce results analogous to those produced by extrusion and "drawing" in the case of the artificial fibres It is natural therefore, having regard for the funnel-like shape of the root in this region, to suspect that here too we have to do with an extrusion phenomenon. The development of the fibrous structure of hair is, however, not an isolated problem. Birefringent structures are common in biological materials and the problem of their formation is therefore of more general interest. The fibrillæ of the precortical cells resemble, and are histologically analogous to, the "tonofibrils" of the epithelial cells of the skin. The arrangement of these fibrils does not suggest any process of extrusion Three main types of theory have been proposed to account for the synthesis of such forms [1] The protein or other substance may be synthesised as long free chains, which are subsequently oriented by some mechanical operation such as, in the present instance, the extrusion of the plastic material through the narrowing neck of the follicle.[2] The chains or some other complex may be synthesised directly in an oriented condition under the influence of some directive force [3] The protein may be formed originally in a relatively symmetrical form and a fibrillar structure result as a secondary aggregation of the "molecules" in the form of long strings as suggested in Figure 2 Observations of the type described in this paper involving measurements of birefringence do not provide the kind of information required to decide which of these theories is applicable to the formation of the cortical material of hair What is really needed is information about the molecular size and shape in the non-birefringent regions of the bulb and attempts are being made to obtain this information. Until it is to hand only a limited discussion of the problem is possible

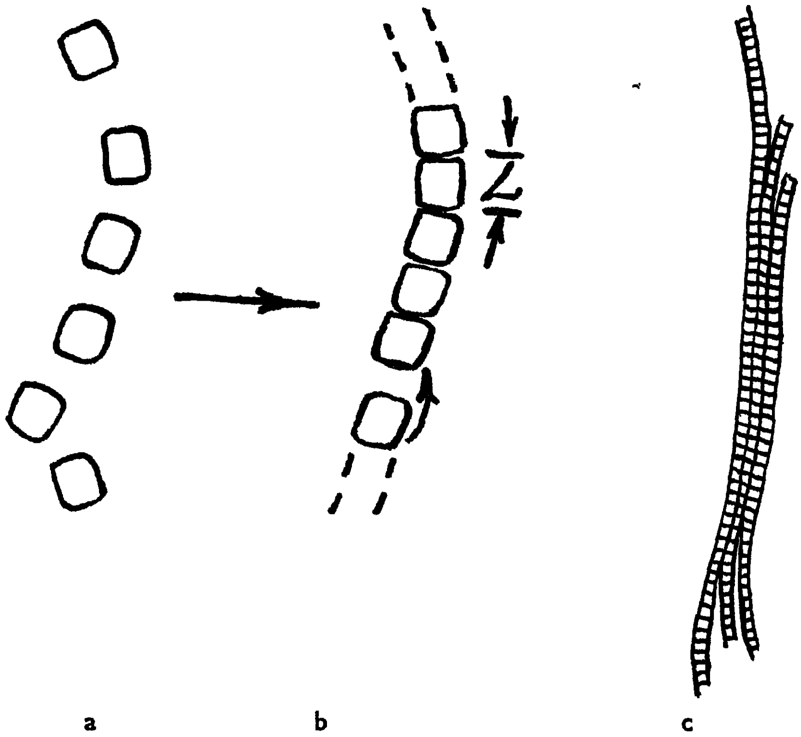

Fig. 2

Hypothetical scheme to explain the formation of birefringent fibrils by the linear aggregation of more symmetrical particles. (*a*) free particles (*b*) formation of linear aggregates (*c*) macrofibrils formed from the proto-fibrils. The periodicity "L" resulting from the regularly recurring particles is a possible cause of the long X-ray spacings

Birefringence measurements are, however, sufficient to show that any theory which attributes the orientation solely to a mechanical extrusion, *e.g.* an extrusion of preformed molecules or fibrils, is untenable. It is to be expected that the amount of deformation, *i.e.* the contraction in area of the root, would determine the degree of orientation in a structure produced by extrusion. In fact the contraction is very variable whereas the DR is an almost constant characteristic. It seems most likely that it is an intrinsic property of the fibrous keratin as is the case with simpler crystals The contraction in area seems to be due rather to the dehydration of the already fibrous protein. At the present time the third theory is enjoying some popularity because electron microscopic examination of several fibrous proteins has shown fibrillar forms which seem to be made up of strings of particles.[14,15] Such a hypothesis has also been used to explain biochemical findings,[16] the existence of long spacings[17] as well as the production of birefringence. The observations made on hair are compatible with it but not of course proof of it. Birefringent fibrils are found in all keratinous tissues and their origin is most easily understood in terms of the particle theory. In hair the peculiarity requiring special explanation is the formation of fibrils parallel to the length of the follicle. It is plausible to suspect here that the slight flow due to extrusion plays an orienting rôle by predisposing the particles to form strings in a definite direction.

THE HARDENING PROCESS

The formation resulting from fibrillation at the level B, although fibrous in the molecular sense, is unstable, and as in the case of artificial fibres it is necessary to harden the protein in order to fit it for the protective purpose it serves. In artificial fibres the procedure is to cross link the protein chains and the hardening of hair is closely analogous. Plucked roots were found to be useful for investigating the problems of hardening also.

The zone of positive thiol reaction (pre-keratin) in the human hair follicle extends from B to E, the region shown dotted in Figure 1.[7] The DR is not sensibly increased subsequent to the level B and therefore hardening must involve changes of minor importance structurally. This would be the case if it were due, as proposed by Giroud and Bulliard, to the modification of side chains only or the joining of chains already closely positioned. The thiol reaction (nitroprusside reagent) is very strong from B to D, and fades from D to E, but it is not of much use quantitatively and gives little indication of the degree of cross linking actually effected at any level. Special tests for stability based on the known behaviour of other protein fibres were therefore tried. These tests make use of the digestibility of the protein by enzymes, the disorienting effects of elevated temperature, and resistance to the attack of acids, alkalis and strong urea solutions.

Enzymes have only a slow action on hair and wool, but digestion is more rapid if the fibre is reduced.[18] When a fresh hair root is dipped into a solution of trypsin (0·05 per cent., *pH* 8 at 40° C.) the bulb is rapidly dispersed and the pre-cortex itself is removed in the course of 2-4 hours for a length BC of about 800 μ above the constriction. Above C the protein swells, but resists digestion for a considerably extended period of time. The inner root sheath is resistant from the level B upwards and the fibre cuticle also may be seen to become resistant before the cortex proper. The appearance of the root after digestion is indicated in Figure 3(b). Evidently a sudden change in the resistance of the cortex occurs at C. The region BC, which is also defined by the other tests to be described, will be referred to as the unconsolidated zone.

The thermal stability of protein fibres is also a useful clue to their degree of consolidation. Rudall[11] in experiments on the extracted pre-keratin found that the stability of fibres of this protein could be varied by the introduction of cross linking. Hair itself is stable at 100° C., but at higher temperatures it contracts, and at the same time the birefringence falls (supercontraction).[19] The contracted fibre yields a partly disoriented β-type X-ray pattern.[17] If now a freshly plucked root is mounted in an inert liquid and warmed to 90° C. for 30 sec. the DR of the region BC, the unconsolidated zone, is completely destroyed as shown in Figure 3(a). Above C it persists indefinitely at this temperature. An X-ray photograph of the zone BC after heating shows that the α-pattern has been replaced by a fully disoriented β-pattern as indicated in Figure 1 at *f*. An interesting point is that disorientation occurs in the zone BC without visible longitudinal contraction of the contents of the follicular lumen. Above this level and at a higher temperature disorientation is accompanied by contraction. This seems to show that one of the consequences of consolidation, which also becomes apparent at C is the establishment of a system of strong links in the direction of the fibre axis. Thermal agitation leading to chain contraction thereafter produces a contraction of the whole macrostructure

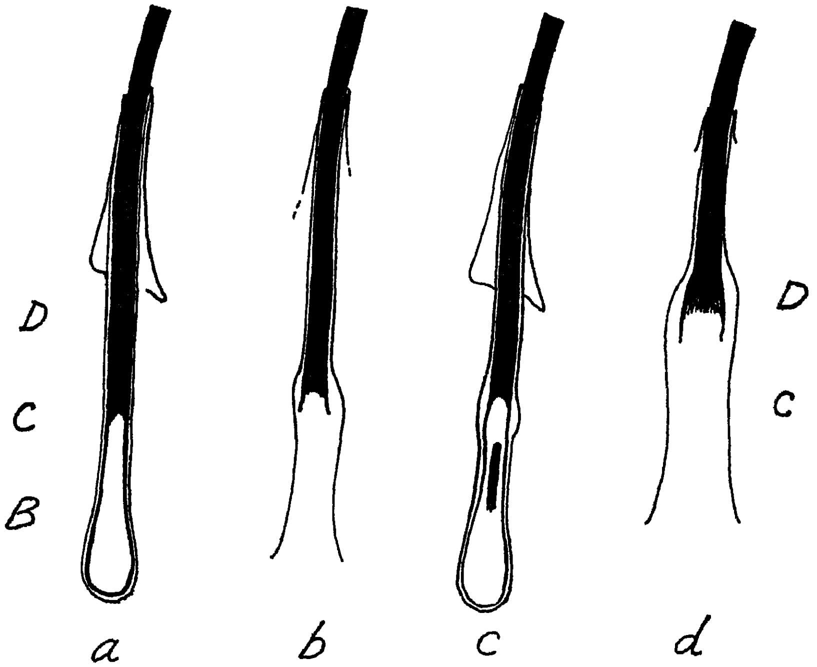

Fig. 3

Histochemical methods of demonstrating the unconsolidated zone BC of the pre-keratin. Birefringent regions are shown in black (*a*) Destruction of orientation in zone BC by heating for 30 seconds at 90°C (*b*) Result of tryptic digestion of a follicle for some hours. BC is removed, the inner root sheath is resistant above the level B and the earlier hardening of the fibre cuticle is apparent (*c*) Destruction of DR due to the penetration of dilute acid (*d*) Result of treatment with dilute alkali which acts destructively even on the partly hardened regions above C

Rudall's use of urea[11] to extract the pre-keratin suggested its use on the follicle The action is spectacular as may be seen from the several stages shown in Figure 4. The bulb region is rapidly dispersed, the nuclei of the cells being released as the cytoplasm dissolves The inner root sheath above B is not dissolved but is distended as the urea penetrates the pre-cortex The birefringent but unconsolidated pre-cortex from B to C is then progressively removed in the course of a few minutes The reagent often attacks at the upper level C at the same time as at the lower level This, however, seems to be a result of plucking as it was not observed in roots treated *in situ* in cow skin. As shown by the other tests described above, hardening begins quite suddenly. Above the fairly definite level C the protein only swells in urea and to a diminishing extent as the consolidation progresses. The production of insolubility and a progressive reduction in swelling power are similar to the behaviour of rubbers as the degree of vulcanisation is increased, and the cause is no doubt similar, *i.e.* the progressive introduction of cross links between the chains.

Giroud and Bulliard[7] have already produced evidence that the cross links are disulphide bridges produced by the oxidation of thiol groups, and support for their view was obtained by observing the results of subjecting the root to reduction If saturated urea containing a few per cent. of a reducing agent, *e.g.* thioglycollate, is used instead of urea in the above experiments, the dispersive action proceeds to an indefinite level above C. The action of dilute alkali, which can also break disulphide bonds, is very similar and the result is shown in Figure 3(d) A follicle may also be reduced in a zinc and hydrochloric acid mixture (saturated with salt to suppress swelling). If a root reduced in this way is dried in alcohol, mounted in oil and warmed to 90° C , as previously described, the destruction of DR now occurs to a level some distance above C. In a complementary way the unstabilised but already oriented lower zone can be cross linked artificially to make it stable towards heating, urea, *etc.* The most effective reagent for this purpose is formaldehyde. Ten minutes immersion in a ten per cent. solution completely hardens the lower levels The X-ray pattern and the birefringence are not altered by this treatment which in this sense also resembles the natural hardening.

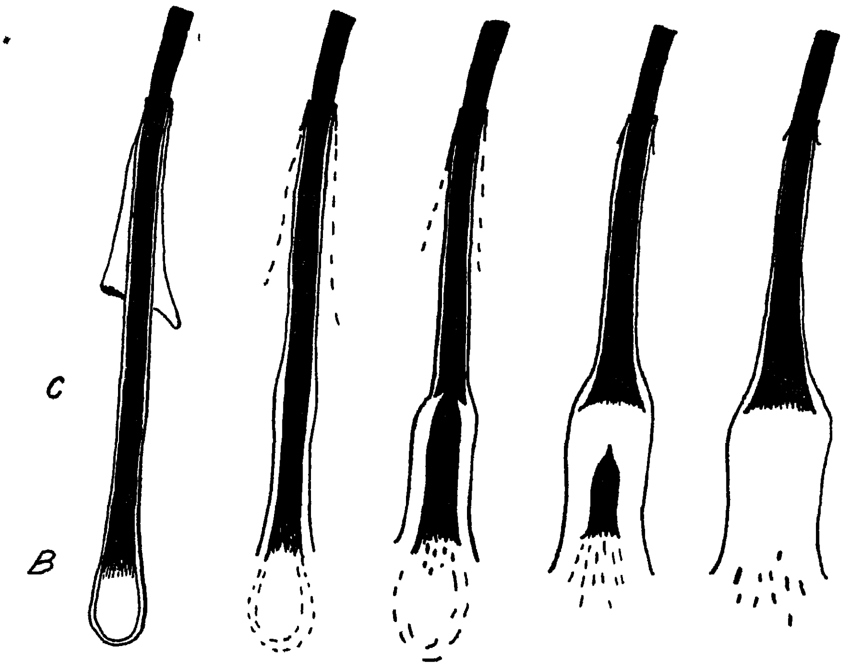

Fig. 4

Progressive dispersion of the unconsolidated pre-keratin by saturated urea. Above C the partly hardened protein swells only and to a diminishing degree as the hardening progresses. Birefringent cortex shown black The time taken for the whole action is 5 to 10 mins

CONCLUSIONS

In conclusion reference may be made again to the analogy which is commonly drawn between the formation of artificial fibres and the growth of hair The analogy is particularly close with regard to hardening, but the great difference between the methods of producing the basic oriented structure in the two cases must be emphasised. There is nothing occurring in the hair root that can be compared with the drawing which is the cause of the greater part of the orientation of artificial fibres. Extrusion appears to play a part but not in a simple mechanical sense It is possible to suppose that the flow produced by extrusion disposes the protein to crystallize in a definite direction. The property of "crystallizing" in fibrils seems inherent, for fibrils occur in all keratinised tissues even in the absence of extrusive forces. The experiments on stability, particularly those involving the use of urea, suggest that the primary fibrils in the unconsolidated zone are held together only by weak energy bonds such as the hydrogen bond or salt links. It is reasonable to suppose that these bonds were responsible for the initial association of the molecules into fibrils. Hardening, which undoubtedly is accompanied by the formation of cystine cross links, does not commence immediately after the formation of the fibrous structure There is a resting period in which no increase in stability can be detected. Although in this region there occur no detected changes, and the DR and X-ray pattern in particular are not modified, it is not unlikely that chemical changes in the side chains preliminary to the cross linking reactions are being effected. All the tests agree that hardening begins quite suddenly and that, in addition to producing insolubility and reducing swelling, it also makes apparent the latent mechanical anisotropy of the oriented molecular structure, probably by forming longitudinal covalent links as well as transverse

SUMMARY

Measurements of birefringence, X-ray examination and special histochemical tests carried out on single hair follicles obtained by plucking from the human head lead to the definition of the following zones in the formation of the cortex of the fibre:

(*a*) *The bulb region*. The protein is soft, isotropic, digestible by enzymes and dispersed by urea. It thus resembles the soluble proteins. Considerable amounts of protein appear to be present in the upper part of the bulb, but the X-ray pattern is diffuse.

(*b*) *The fibrillation zone at the constriction of the follicle*. The protein becomes birefringent to the same degree as the final hair in a single stage. X-rays show that subsequent to this level the α-keratin structure of the final hair is present

(*c*) *The unconsolidated pre-keratinous zone*. This zone and the next are characterised by a positive thiol reaction. The structure, although fully oriented, is still unstable. Urea rapidly dissolves it, moderate temperatures lead to disorientation with a fall in birefringence, but without a contraction in the longitudinal direction of the shaft. After heating the zone yields a disoriented β-pattern. The zone can be stabilised by the introduction of artificial cross linking.

(*d*) *The zone of consolidation* Hardening becomes detectable about halfway along the "pre-keratinous region" and is thereafter progressive. Above

a fairly definite level the protein only swells in urea, is not digested by enzymes, and is not disoriented at 90° C. Heating to a higher temperature causes disorientation with a contraction in length.

(*e*) *The fully hardened hair*

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REFERENCES

[1] Hill *Trans. Faraday Soc*, 1933, 29
[2] Woods *Proc Roy. Soc.*, 1938, 166A, 76
[3] Mercer *J Counc. Sci Res Aust*, 1942, 15, 221.
[4] Maximov and Bloom. *Textbook of Histology*, 1936
[5] Astbury and Woods *Phil Trans Roy Soc*, 1933, 232A, 333
[6] Astbury Croonian Lecture *Proc Roy Soc. B*, 1947, 134, 303 (Review)
[7] Giroud and Bulliard *Archives de Morphologie*, 1930, 29.
[8] Speakman *J. Soc. Dyers and Colourists*, Jubilee Issue, 1934 (Review)
[9] Harris and Brown *Symposium on Fibrous Proteins J. Soc Dyers and Colourists*, 1946, 15, 203
[10] Marston *Ibid*, p 207
[11] Rudall. *Ibid*, p 15
[12] Mercer Thesis for Ph D, Leeds University, 1949, *Nature*, 1949, 163, 18
[13] Schmidt *Die Bausteine des Tier Korpers*, 1924. *Handb der Biol. Arbeitsmethode*, 1938, Abt. 5, Teile 10, 588.
[14] Jakus and Hall *J Biol Chem*, 1947, 167, 705.
[15] Astbury, Perry, Reed and Spark *Biochem & Biophys. Acta*, 1947, 1, 379
[16] Szent-Gyorgyi *Chemistry of Muscle contraction*, 1947
[17] Elod, Nowotny and Zahn *Mell Textilber*, 1944, 25, 73
[18] Hock et al *Text Res J.*, 1940, 11, 45.
[19] Schmidt *Zeit Zellforschung Mikros Anat.*, 1932, 15, 188

38—EFFECT OF PRELIMINARY HYDROLYSIS ON THE DETERMINATION OF LIGNIN IN JUTE

By A. B. SEN GUPTA and H. J. CALLOW

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INTRODUCTION

Of the methods suggested for determining lignin in plant materials, the most widely used is that in which the material is treated with 72 per cent. sulphuric acid and, after dilution and boiling, the residue is filtered off and weighed as lignin. But even this method has a number of defects. The production of an insoluble residue from the polysaccharides during treatment with mineral acid appears to be the cause of a high apparent yield of lignin. Norman and Jenkins[1] suggest that this higher yield is due to the formation of a condensation product between lignin and furfural obtained from pentoses and in order to obtain a more nearly correct value, Norman[2] has advocated that "either the conditions may be so modified that the production of furfuraldehyde or other reactive fission products is at a minimum, or the constituents containing pentose which might give rise to furfuraldehyde may be removed by a suitable pre-treatment . . ." This latter proposal, *viz.* removal of pentose-containing polysaccharides, has been applied by a number of workers and is generally accomplished by hydrolysing the material with dilute acids Various concentrations of acid and different times of boiling have been suggested; 5 per cent. sulphuric acid for 1 hour[1] or 1 per cent. hydrochloric acid for 3 hours[3] are typical examples Some doubt, however, exists as to whether this type of pre-treatment is accompanied by a loss of lignin through partial solubility in the dilute acid, the work of Cohen and Harris[4] indicates that partial solution of lignin takes place during hydrolysis of samples of wood.

During a study of the conditions necessary for progressive delignification of jute fibre without removing the hemicellulosic constituents, a method was required for determining the lignin contents of the treated samples As a result of such treatment, the ratio of xylan to lignin in the untreated jute is increased considerably and it was therefore proposed to examine the effect upon the lignin yield of untreated jute to which large amounts of xylan had been added. At the same time, a comparison was made of the yields of lignin from unhydrolysed and hydrolysed samples of jute, the hydrolysis being carried out with 5 per cent. sulphuric acid An acid hydrolysis of this kind is believed by Norman and Jenkins[1] to give a more accurate value from a large number of plant materials. During the present investigation the determination of lignin was carried out at a lower temperature than that used by Norman and Jenkins[1] (about 20° C.) because there is then less possibility of condensation products being formed, and a temperature of 2° C was used throughout. The minimum time necessary for removing the carbohydrates at this temperature was first ascertained and the effect of adding xylan to both unhydrolysed and hydrolysed jute upon the yield of lignin at 2° C was then examined In addition, the investigation was extended to discover if any lignin was removed from jute during the preliminary hydrolysis.

EXPERIMENTAL

Material. Jute fibre (white jute, Niklidampara) was washed with water to remove dirt and easily soluble matter, dried at room temperature, ground to powder in a Christie and Norris high speed mill and that portion which passed a 72-mesh sieve retained for analysis. After extraction with an alcohol-benzene mixture (1:2, v/v), the powder was washed with alcohol to remove benzene, dried in room air and conditioned at 22° C. and 65 per cent. relative humidity.

Method of determining lignin. Jute powder (2 gm. conditioned weight*) was treated in a 100 ml. beaker with 72 per cent. sulphuric acid (25 ml.), previously cooled to 2° C., and kept at that temperature for different periods, the contents being occasionally stirred to avoid the formation of lumps. The resulting mixture was diluted to 600 ml., refluxed for 2 hours and, after cooling, the insoluble material was collected on a tared, sintered glass crucible (1G3), washed with cold water until free from acid, dried at 105° C. and weighed as lignin. The means of duplicate determinations with different times of treatment are shown in Table I.

Table I
Effect of time of treatment on the yield of lignin at 2°C.

Time of treatment (hours) ...	12	24	36	48	72	96
Lignin (%) ..	18·32	14·52	13·07	13·08	13·33	13·58

After 12 and 24 hours' treatment the material was very difficult to filter, the results of duplicate experiments varied considerably and the high values which were obtained indicated that removal of carbohydrates was incomplete. The material could be filtered readily after a minimum treatment of 36 hours and good duplicate values were obtained. The results shown in Table I also indicate that the yield of lignin reaches a minimum after 36 to 48 hours' treatment and during the subsequent experimental work, treatment for 48 hours was adopted as the standard procedure.

Effect of adding xylan to jute powder on the yield of lignin. Powdered jute was intimately mixed with different proportions of isolated jute cellulose containing xylan and the yield of residue determined after treating for 48 hours with 72 per cent. sulphuric acid at 2° C. The cellulose was isolated from the original fibre by treating this with chlorine dioxide solution, extracting with sodium sulphite solution,[5] washing, drying and grinding to powder. That portion passing through a 72-mesh sieve was then extracted with an alcohol-benzene mixture, washed with alcohol and dried in room air. The xylan content of this cellulose fraction was 14·92 per cent. as determined by the gravimetric phloroglucide method of Angell, Norris and Resch[6] and the "lignin" content, determined by treatment with 72 per cent. sulphuric acid at 2° C. for 48 hours, was 0·045 per cent. A known weight of the conditioned jute powder was then mixed with a known weight of the conditioned cellulose powder so that the total dry weight of the mixture was approximately 2 gm. The lignin contents were determined as before, the results being shown in Table II. From these results it appears that the addition of xylan in the form of "total cellulose" has no significant effect on the yield of lignin under the conditions of the experiment. It may be that either the lower temperature at which these experiments were carried out is not favourable to the formation of condensation products or that the amount of xylan which is present in jute is sufficient to form the maximum amount of condensation product with the lignin. The latter reason, however, does not seem to be tenable, because Norman[2] has reported a considerable increase in the yield of lignin after the addition of crude xylan to unhydrolysed straw, and in jute a similar behaviour might be expected.

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* Throughout this work, the percentage of lignin is expressed on the weight of jute dried at 105°C. Moisture contents were determined on separate samples.

Table II
Effect of added xylan on the yield of lignin from jute

Dry weight of jute powder (gm.)	Dry weight of cellulose powder (gm.)	Lignin (%)*	
1·4440	0·5287	13·11	13·07
1·4490	0·5252	13·02	
0·9972	1·0560	13·03	13·03
0·9942	1·0316	13·02	
0·5473	1·5569	13·06	13·01
0·5341	1·5701	12·96	

* Expressed as a percentage of the dry weight of jute in the mixture

Effect of hydrolysis upon the yield of lignin from jute. Analytical procedures for the determination of lignin have always been based upon obtaining the lowest yield of residue. Despite the reproducible results obtained in the previous experiment, it is not known whether the value of lignin obtained is an accurate one, especially as Norman[1] has shown that a lower value is obtained by pre-treating lignocellulosic material with 5 per cent. sulphuric acid. This lower value may be due either to the prevention of condensation reactions which lead to the formation of acid-insoluble products or to partial solution of the lignin in the acid used for hydrolysis. In order, therefore, to obtain some clue as to the rôle played by hydrolysis on the lignin yield, the effect of such a hydrolysis and the influence of adding cellulose (containing xylan) to hydrolysed jute was then examined.

The hydrolysis was carried out by refluxing jute powder (2 gm.) with 5 per cent. sulphuric acid (200 ml.) for 1 hour, the extracted material being filtered through a sintered glass crucible (1G3) and washed with hot water until free from acid. It was dried at 105° C., weighed and the lignin determined as before. The low yield of residue (equivalent to 10·80 per cent. of the dry weight of jute) shows that a considerable reduction in the yield of lignin follows hydrolysis with dilute sulphuric acid. According to Norman (*loc. cit.*), this reduction is due to removal of pentose materials, but Cohen and Harris (*loc. cit.*) have obtained results which suggest that some lignin is dissolved during a pre-treatment of the above nature.

Whilst, as shown above, isolated cellulose containing xylan, forms only a negligible insoluble residue (0·045 per cent.) when treated with strong sulphuric acid at 2° C., it is possible that fission products derived from the xylan would, in the presence of lignin, form insoluble condensation compounds. In order to examine for this possibility, a known weight of jute was extracted with 5 per cent. sulphuric acid for 1 hour, washed, dried and mixed with unhydrolysed cellulose powder so that the total weight of cellulose and original jute was approximately 2 gm. The mixture was treated with 72 per cent. sulphuric acid at 2° C. and, as shown in Table III, there is a very small increase in the yield of lignin in only one case. This increase, however, is far less than the reduction brought about by the hydrolysis.

Since, in the above experiment, the amount of xylan added in the form of cellulose to the hydrolysed jute was considerably less than that which was present in the original unhydrolysed jute, it was next decided to add more xylan to hydrolysed jute with a view to replacing quantitatively the removed furfural-yielding bodies. Thus, jute powder having a furfural content of 9·72 per cent. gave 2·46 per cent. furfural after acid hydrolysis and the calculated amount of cellulose powder, with a furfural content of 9·47 per cent., was added to the hydrolysed jute in order to replace the furfural-yielding bodies which had been removed during hydrolysis. The lignin content of this mixture was 10·93 per cent., a value which does not differ appreciably from that of the hydrolysed jute (10·80 per cent.). It appears from these values that the lowering of the lignin value from 13·08 per cent. to 10·80 per cent. by acid extraction is due largely to solubility of the lignin in the acid and an examination of the acid extract was therefore made in order to see if lignin (or its degradation products) could be detected. Jute powder (2 gm.) was refluxed with 5 per cent. sulphuric acid and the filtrate and washings were made up to 250 ml. A portion (25 ml.) of the solution was treated with dilute chlorine dioxide solution for 3 hours and the excess chlorine dioxide determined iodimetrically and it was found that the amount of chlorine dioxide consumed by the extract from 2 gm. of jute was 0·047 gm. Since chlorine dioxide is reported to have no action on carbohydrates,[7] this consumption of chlorine dioxide is likely to be due to the presence of either lignin or its degradation products in the extract. The remaining portion (200 ml.) of the above extract was neutralised with barium carbonate, the barium sulphate filtered off, and the filtrate evaporated to dryness on a water bath before being finally dried at 105° C. The dried residue was treated with 72 per cent. sulphuric acid at 2° C. for 48 hours, diluted to 3 per cent. acid concentration and refluxed for 2 hours, the insoluble residue being collected in a 1G4 sintered crucible, washed with water and dried at 105° C. After applying a correction for the inorganic impurities by dissolving the organic portion in hypochlorite solution, a recovery of 73·2 per cent. of the "lignin" lost during the acid pre-treatment was obtained.

Table III
Effect of adding cellulose to hydrolysed jute on the yield of lignin

Composition of mixture		Loss in weight of jute on hydrolysis (%)	Lignin on original jute (%)	
Hydrolysed jute (%)	Isolated cellulose (%)			
100	0	21·89	10·78	10·80
100	0	21·87	10·82	
66·87	33·13	21·04	11·20	11·14
67·27	32·73	20·89	11·08	
42·50	57·50	21·12	10·94	10·88
43·30	56·70	21·19	10·81	

Methoxyl content of isolated lignin. Since methoxyl groups are characteristic of lignin, it was decided to determine the methoxyl contents of lignin isolated from jute before and after acid hydrolysis and to compare the values with that of the solid isolated from the acid extract. This solid was obtained by neutralising the extract with caustic soda solution, evaporating to dryness and treating the residue with 72 per cent. sulphuric acid for 48 hours at 2° C., diluting to 3 per cent. acid content and refluxing. All the methoxyl values were determined by a modification of the Zeisel method, and consisted of oxidising the methyl iodide, evolved on distillation with hydriodic acid, with bromine and determining the amount of iodic acid so formed.[8] Finely powdered, dry lignin (0·1 gm.), and finely powdered solid isolated from the 5 per cent. sulphuric acid extract, were treated with phenol

(7·5 gm.) and hydriodic acid (12 ml.) for 1 hour at 135° C. as in the method described by Clark[9] and the values obtained are given in Table IV. It is noted that the methoxyl contents of the lignin isolated before and after hydrolysis are identical, a result which would not be expected if the sole function of the preliminary hydrolysis was to remove furfural-yielding substances and so prevent condensation between furfural and lignin. The effect of diluting the lignin by allowing a condensate between furfural and lignin to form would be to decrease its methoxyl content, and if the formation of a condensate of this type were prevented, the methoxyl content of the residue would increase. But this is not observed in practice and taken in conjunction with the fact that the solid isolated from the acid extract has a methoxyl content only slightly lower than those of the isolated lignins, supports the view that a portion of the lignin has been removed during acid hydrolysis and can be recovered from the acid extract. The lower methoxyl content of this solid may be due either to an original small intrinsic difference in substituent groups, as suggested by Norman,[10] or to a loss of methoxyl groups during isolation as reported to take place by Heuser and Wenzel.[11]

Table IV

Material	Methoxyl content (%)
(*a*) Lignin isolated from jute without pretreatment .	18·81
(*b*) Lignin isolated from jute after pretreatment . .	18·80
(*c*) Solid isolated from 5% sulphuric acid extract	16·03

X-ray photographs of the two isolated lignins and of the solid obtained by the acid extract were taken and the diagrams were found to be identical. Since, in addition, the solid obtained from the acid extract reacts with chlorine dioxide, gives a positive colour test for lignin (Maule test) and carries a high proportion of methoxyl groups, it seems likely that the product is lignin.

During the above work, pre-treatment had been carried out using one strength of sulphuric acid (5 per cent.) at a fixed liquor ratio (100 : 1). In order, however, to examine the effect of other liquor ratios and times of treatment on the lignin yield, jute was extracted using the conditions shown in Table V. These have only a small effect on the lignin content of the hydrolysed jute and the results suggest that only a part of the lignin originally present is removable during hydrolysis with dilute acid.

Table V

Effect of liquor ratio and time of boiling on the lignin yield

(Lignin content of original jute, 13·08%)

Liquor ratio	Time of treatment (hours)	Lignin (%)
100 : 1	1	10·80
400 : 1	1	10·67
400 : 1	2	10·62

DISCUSSION

Treatment of jute with 72 per cent. sulphuric acid at a temperature of 2° C. gives a minimum yield of lignin after 36 to 48 hours. The slight progressive increase in this yield which is noted after prolonging the time of treatment is, in all probability, due to formation of condensation products between furfural and lignin. Despite the reproducibility of results after treatment for 48 hours at 2° C., it was not known whether the value obtained was an accurate one, because Norman[1] has shown, in the case of straw, an increase in the yield of residue when pentosans are present and the reaction is carried out for 16 hours at a temperature in the neighbourhood of 20° C. The modification introduced by Norman[1] for the accurate determination of lignin was to remove the pentoses by hydrolysing with 5 per cent. sulphuric acid prior to treatment with 72 per cent. sulphuric acid. On hydrolysing jute, however, the yield of lignin decreased from 13·08 per cent. to 10·80 per cent. No increase in the lignin value was observed when xylan, in the form of total cellulose, was added to hydrolysed or unhydrolysed jute thus indicating that, in addition to removing pentoses, some of the lignin was eliminated during the hydrolysis. The acid extract was found to react with chlorine dioxide and on neutralising, evaporating to dryness, and subjecting to the normal process used for determining lignin, gave a solid which contains 16·03 per cent. methoxyl. This value is only slightly lower than those obtained for isolated lignins and since the solid isolated from the acid extract reproduces the X-ray diagram of and gives the characteristic colour test for lignin, it appears extremely likely that it is a soluble form of lignin.

As only a fixed amount of lignin could be removed from the fibre by acid pre-treatment, it seems most likely that there are two types of lignin present in jute, one being soluble and the other insoluble in dilute acid. In relation to this possibility, Preston[12] has noted that during the water-retting of jute under carefully controlled conditions, lignin is removed easily from the primary wall while the secondary wall remains strongly lignified The suggestion is made, therefore, that in the production of the retted fibre of commerce to which this work relates, some of the lignin in the primary wall is still retained and that it is this portion of the lignin which is removed during pre-treatment with dilute acid Since, as shown by Preston,[12] the secondary wall does not undergo swelling, even in the presence of strong mineral acid, it is unlikely that a pre-treatment with 5 per cent sulphuric acid will dissolve lignin from this region

For the determination of lignin in jute fibre, hydrolysis with 5 per cent. sulphuric acid prior to treatment with 72 per cent acid not only removes pentoses but also dissolves a portion of the lignin. A more correct value is obtained, therefore, without such a pre-treatment

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REFERENCES

[1] Norman and Jenkins *Biochem J*, 1934, 28, 2147
[2] Norman. "The Biochemistry of Cellulose, the Polyuronides, Lignin, etc." Oxford, 1937, p 171
[3] Goss and Phillips. *J Assoc. Off Agr. Chem.*, 1936, 19, 341.
[4] Cohen and Harris *Ind. Eng Chem, Anal Ed*, 1937, 9, 234.
[5] Dorée "The Methods of Cellulose Chemistry," 1947, p 360
[6] Angell, Norris and Resch. *Biochem. J.*, 1936, 30, 2146
[7] Schmidt and Graumann *Ber.*, 1921, 54, 1860
[8] Dorée. "The Methods of Cellulose Chemistry," 1947, 399-403.
[9] Clark. *J. Amer Chem Soc.*, 1929, 51, 1480
[10] Norman. "The Biochemistry of Cellulose, the Polyuronides, Lignin, etc" Oxford, 1937, p. 151
[11] Heuser and Wenzel *Papier Fabrik*, 1921, 19, 1183.
[12] Preston. *Proc. Roy Soc.*, 1941, *B.*, 130, 103-112

39—REDUCTION OF THE WORSTED OPEN DRAWING PROCESS

By P. P. Townend and M. Z. Rzegocinski

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INTRODUCTION

The present trend in worsted yarn production is to reduce the work entailed in the conversion of top to roving and yet maintain the standard of the product. If the present weight per unit length of top is retained then a reduction in the number of processes can be effected only by reducing the doublings[1] or increasing the draft[2] at each operation; both have been shown to be possible and practical. A third method of reducing the number of drawing operations might be achieved if it could be shown that a much lighter top can be used. Normally the Noble comb produces a comb sliver weighing, for botany wools, 1½ ounces per 10 yards. About twenty of these slivers are fed to the 1st finisher gill with a draft of four to give a sliver weighing 8 ounces per 10 yards, two of which are fed to the 2nd finisher gill with a draft of just below four to give the resultant top weighing 4¼ ounces per 10 yards The practical difficulties of using the comb sliver as top are due first to the organisation of the worsted industry wherein a spinner does not himself comb but buys tops from the comber; the top must therefore be of a transportable nature Secondly, the comb sliver is not so regular in weight along its length as the finished top Nevertheless, it was thought that an investigation into the possibilities of using a comb sliver as top would be worth while.

EXPERIMENTAL

One hundred pounds of 64s Australian greasy wool, warp type, was scoured, carded, backwashed, gilled and punched prior to combing Carding was effected in the damp state on a four licker-two swift Bradford type botany card. During backwashing three per cent. of Topsol, by weight on the wool, was added Combing was carried out on the Noble comb, the finest pinning being 42 and 46 pins per inch. Usually the sliver delivered by this machine, processing 64s wool, weighs 100 drams per 40 yards (1½ ounces per 10 yards), but in this instance the sliver was brought off weighing 80 drams because this was the weight of slubbing normally fed to the 2nd finisher drawing machine where it was hoped to introduce the sliver into the drawing process This lighter sliver was made by speeding up the drawing, the three dram roving was spun on a Parawind ring frame to 1/36s scheme of processing, to the end of combing, is summarised in Table I.

Table I

Process	Doublings	Draft	Weight (oz /10 yards)
Scouring . .	—	—	—
Carding	—	—	3 6
Backwashing . .	12	4	10·7
1st strong box . ..	6	4	16
2nd strong box .	4	4	16
Punch .	—	—	—
Noble comb . .	—	—	1·25

The slivers, on issuing from the comb, were divided into three lots, cans 1, 4, 7, *etc.*, going to form lot A, cans 2, 5, 8, *etc.*, to form lot B, and cans 3, 6, 9, *etc.*, to form lot C.

Those forming lot A were converted by the ordinary finishing process to a normal top, sixteen slivers being doubled at the 1st finisher gill and three at the 2nd finisher gill with a draft of four, to give a top weighing 240 drams per 40 yards. Top A was then reduced to a 3 dram roving using the drafts, doublings and operations normally associated with this type of wool. These, together with the top finishing process, are set out in Table II where it will be seen that eight drawing operations were used, the first one, at the can gill, being used for further mixing and regularising. The drafts, throughout the process of reduction, were in no way excessive, ranging from 4 to 6·1. After drawing, the three dram roving was spun on a Parawind ring frame to 1/36s worsted count, 15 *t.p.i.* (calculated).

Table II

Operation	Doublings	Draft	Weight (drams per 40 yards)
1st finisher gill	16	4	320
2nd finisher gill	3	4	240
Can gill	4	4	240
Spindle gill	4	5·1	190
1st drawing	4	5	152
2nd drawing	4	5	122
1st finisher	4	6	82·5
2nd finisher	2	6·2	27
Reducer	2	5·9	9·2
Rover	2	6·1	3·0
Ring spinning frame	1	5·9	0·5 (1/36s)

In the case of lot B the top finishing process, and therefore any thickening of the sliver, was omitted. Instead the combed sliver was gilled on the can gill,* four ends up with a draft of four, so that the sliver weight remained the same, *viz.*, 80 drams per 40 yards The material was passed through the machine four times after which the gilled sliver was taken to the 2nd finisher drawing machine for reduction to roving The weight fed to this machine was therefore the same as in the case of lot A. Normally the twist necessary for fibre control in the subsequent drafting process is imparted by the previous machine, but since in this case the sliver was twistless it had first to be passed through the front rollers only and wound on to the bobbin of the 1st finisher drawing machine. The twisted sliver was then drawn on the 2nd finisher followed by the reducer and roving frames, to be spun finally on the same machine as lot A to the same count and twist. The processing details of lot B from comb sliver to yarn are given in Table III.

Table III

Operation	Doublings	Draft	Weight (drams per 40 yards)
Can gill	4	4	80
Can gill	4	4	80
Can gill	4	4	80
Can gill	4	4	80
2nd finisher	2	5·9	27
Reducer	2	5·9	9
Rover	2	6·1	3
Ring spinning frame	1	5·9	0·5(1/36s)

---

* The can gill box was used instead of the finisher gill box because of ease of manipulation

The combed sliver forming lot C was processed in a similar manner to that of lot B except that it was passed once only through the can gill, after which it was reduced and spun. Processing details from comb sliver to yarn are given in Table IV.

Table IV

Operation	Doublings	Draft	Weight (drams per 40 yards)
Can gill	4	4	80
2nd finisher	2	5·8	27
Reducer	2	6	9
Rover	2	6·2	3
Ring spinning frame	1	5·9	0·5 (1/36s)

Figure 1 illustrates in graphic form the number of operations used in each process and the changes in weight per unit length during conversion from combed sliver to spun yarn The height of each strip is proportional to the weight of 40 yards of sliver, the white portions representing the weight of sliver delivered by the machine whilst the shaded portions represent the weight fed to the machine. At the same time Table V has been drawn up to show the total draft and doublings imposed on each lot. It will be seen that these were comparatively few in the case of lot C, more in lot B and very many in lot A.

Table V

	A	B	C
Total doublings from comb to spun yarn .	393,200	2,048	32
Total draft from comb to spun yarn	64,450,000	320,800	5,093

EXAMINATION OF PRODUCT

Uniformity of Combed Sliver and Top

Examination of the long term, as opposed to short term, variations in sliver, top, roving and yarn was effected by cutting successive lengths of sliver, *etc.*, and weighing them on an automatic balance. It was decided to cut and weigh successive twelve-inch lengths of the comb slivers and then to use a test length for the top, rovings and yarns which gave the same weight. Besides allowing a comparison of the three processes, this procedure showed the effect of draft on the regularity of a mass of fibres during their attenuation by the drafting process.

During combing three portions of the sliver were collected at intervals throughout the run, samples were also taken from lot A after the top finishing process, from lot B after the fourth passage through the can gill and from lot C after its one passage through the can gill. These were stored under constant temperature and humidity conditions for three days prior to being cut into lengths and weighed. Since top A was three times as thick as the other slivers, it was cut into four-inch lengths so that the test piece should be the same weight. The mean weights and coefficients of variation obtained for the different products are given in Table VI, whilst Figures 2, 3, 3a, 4 and 5 show the measure of irregularity. In order to extract the most information from top A, the weights of successive four-inch lengths have been grouped in threes to give the weights of successive twelve-inch lengths. These results are included in Table VI.

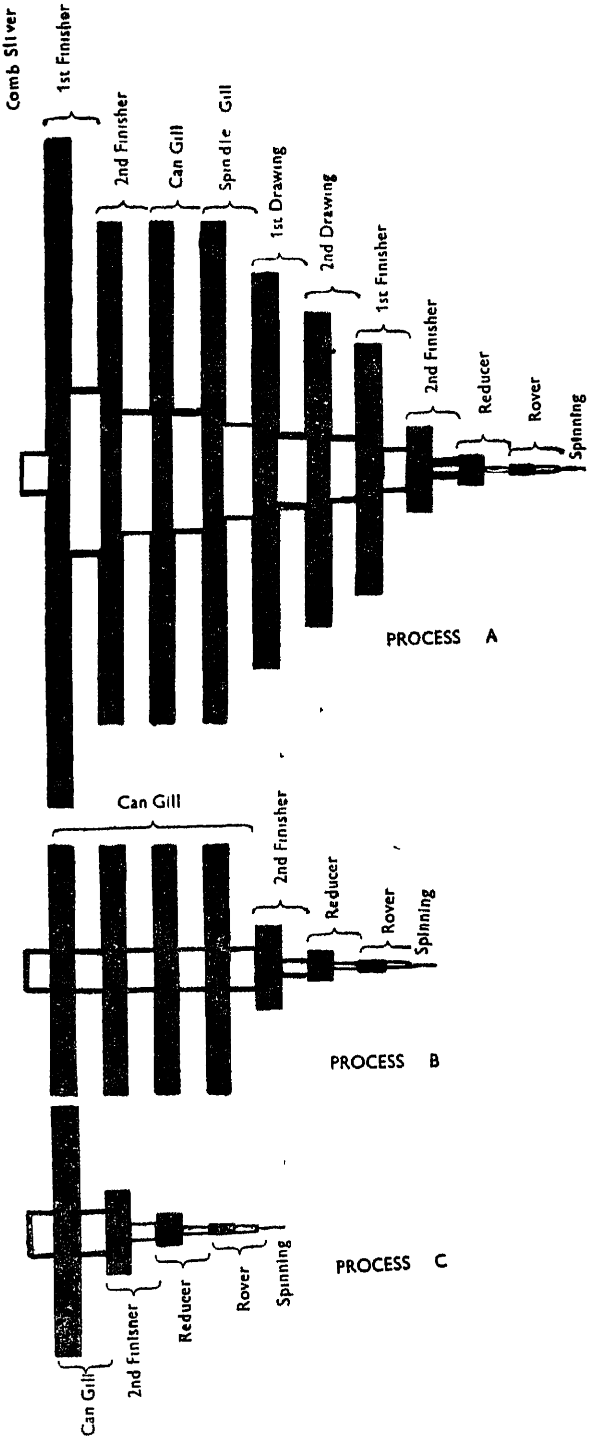
Comb Sliver
1st Finisher
2nd Finisher
Can Gill
Spindle Gill
1st Drawing
2nd Drawing
1st Finisher
2nd Finisher
Reducer
Rover
Spinning
PROCESS A
Can Gill
2nd Finisher
Reducer
Rover
Spinning
PROCESS B
Can Gill
2nd Finisher
Reducer
Rover
Spinning
PROCESS C

Fig. 1

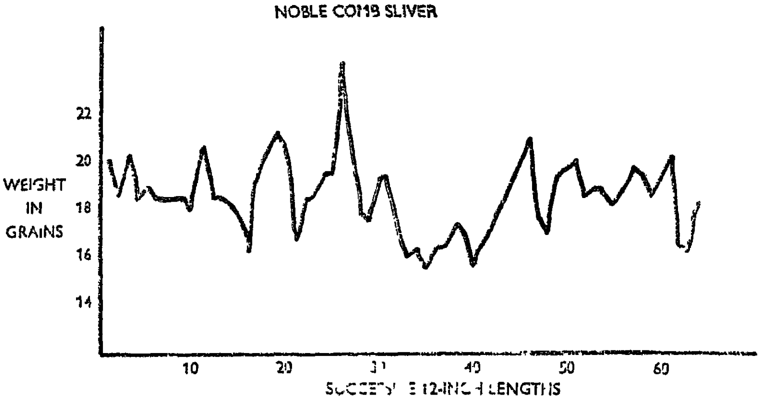

Fig. 2

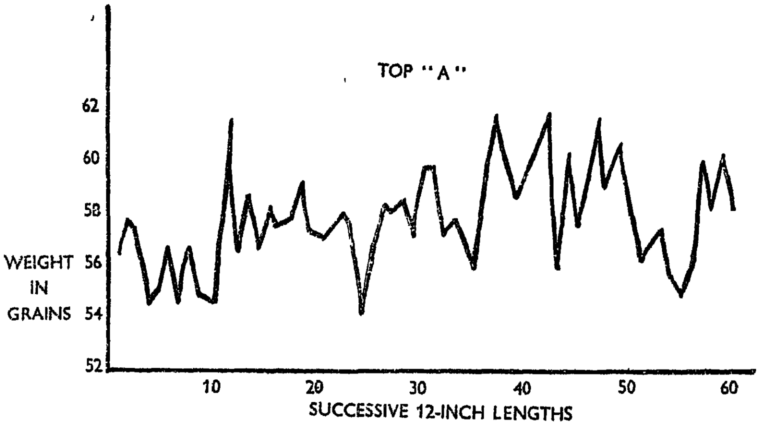

Fig 3

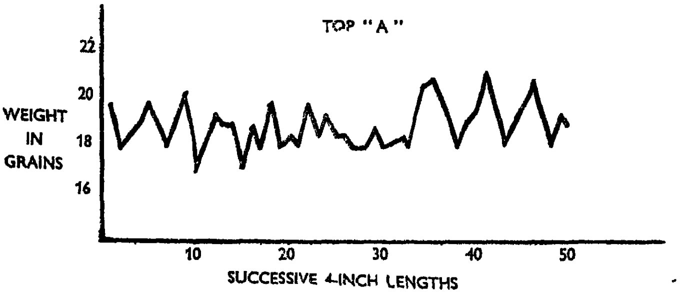

Fig 3a

Table VI

Product	Drams/40 yards	Number of observations	Length weighed (in.)	Mean weight (grains)	Coefficient of variation %
Comb sliver ...	80	192	12	19·2	10·4
Top A . . .	240	61	12	57·8	3 7
Top A .	240	184	4	19 5	5·2
Top B	80	167	12	18·3	5·6
Top C .. .	80	120	12	18 5	7·1

Comparing the figures obtained for the coefficients of variation of the sliver and tops it is evident that the gilling process has reduced the variation in the original sliver. Top C which had been subjected to one gilling process only with four ends is considerably more uniform than the comb sliver, whilst Top B in turn, as a result of four gillings, is more uniform than Top C. Considering the coefficient of variation of the 12-inch lengths it is interesting to observe that Top A, which was subjected to two gillings only, is more uniform than Top B after four gillings. This increase in uniformity of Top A must be attributed to the extra doublings (16) which this material received at the 1st finishing gill.

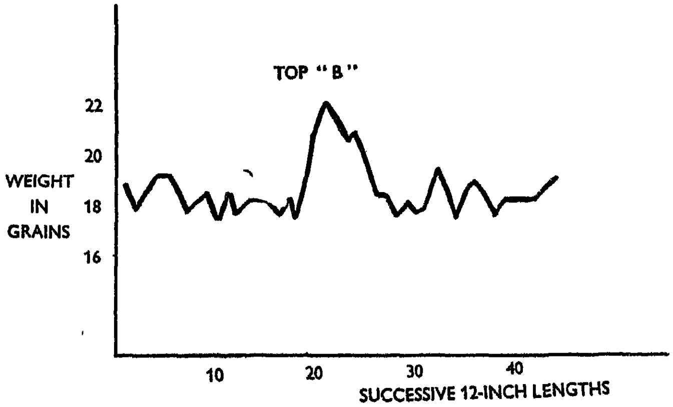

Fig. 4

Before the three tops were drawn analyses were made for fibre length distribution by the cut square method.[3] Three samples were taken from each top, each consisting of approximately 250 fibres. The percentage frequencies together with mean fibre length and standard deviation are given in Table VII.

Table VII

Length (cm)	Frequency (%)		
	Top A	Top B	Top C
0– 1	2·6	2·3	1·8
1– 2	7·5	2·4	2·4
2– 3	8·3	6·3	6·5
3– 4	10·4	11·1	10·1
4– 5	11·7	12·4	12·1
5– 6	11·5	11·1	10·6
6– 7	11·7	11·5	11·1
7– 8	10·7	10·3	11·1
8– 9	8·8	8·7	10·0
9–10	7·4	8·6	8·1
10–11	4·3	7·3	5·7
11–12	2·3	3·9	5·9
12–13	1·3	2·1	2·1
13–14	0·8	1·7	0·9
14–15	0·1	0·7	0·5
15–16	0·1	—	0·3
16–17	—	—	0·1
Mean fibre length (cm.)	6·0	6·6	6·7
Standard deviation ..	2·8	3·3	3·2

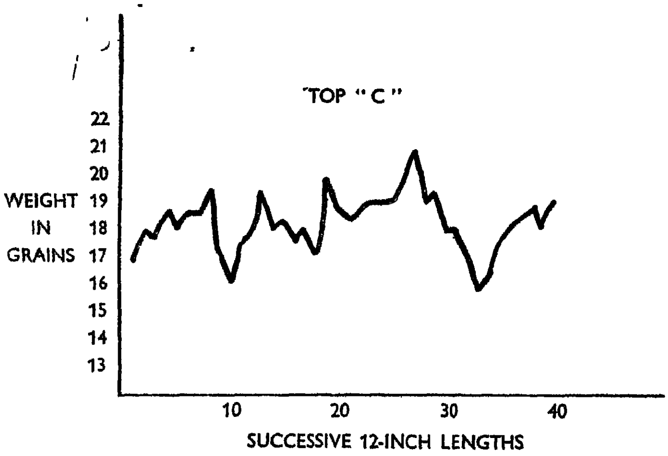

Fig. 5

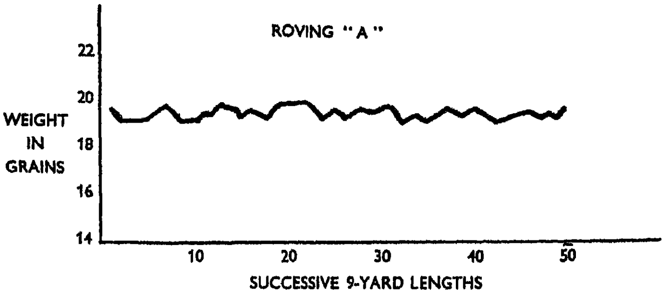

Fig 6

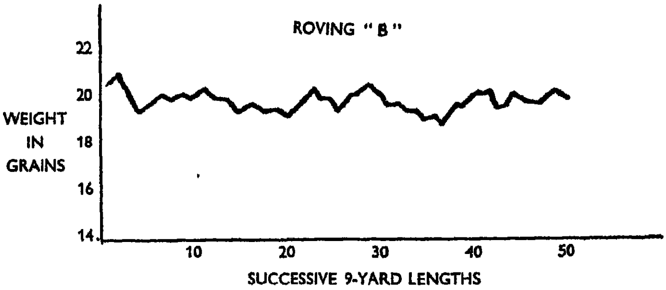

Fig 7

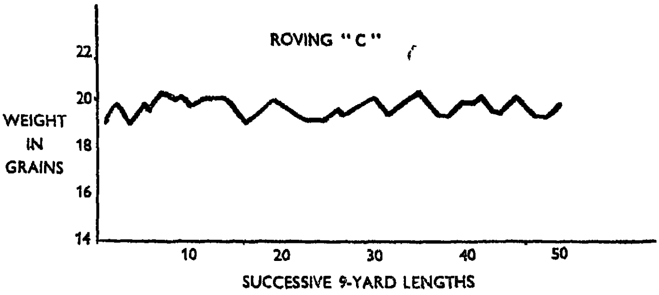

Fig 8

The mean fibre lengths of the three tops, together with the frequency distributions, show that Top A suffered more breakage in gilling than the other two tops. This might be due to the fallers being more densely crowded in the 1st finishing operation when sixteen ends were fed to the machine than in the case of lots B and C, so that a greater force had to be exerted in pulling the fibres forward by the front rollers.

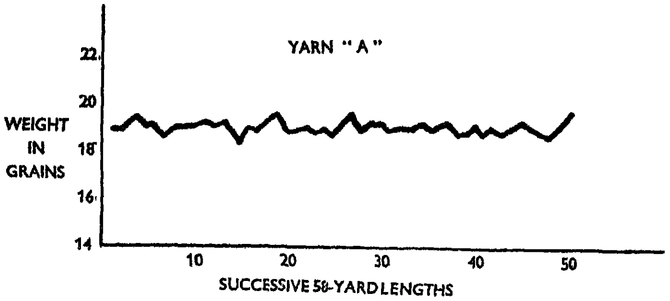

Fig 9

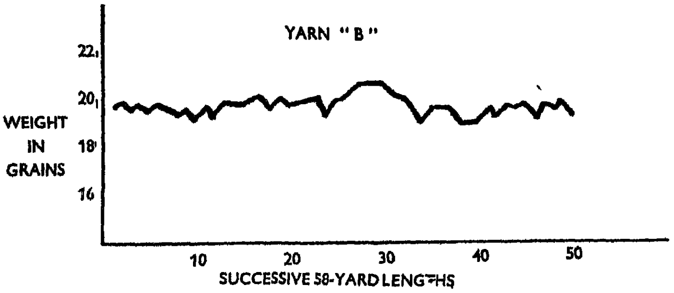

Fig. 10

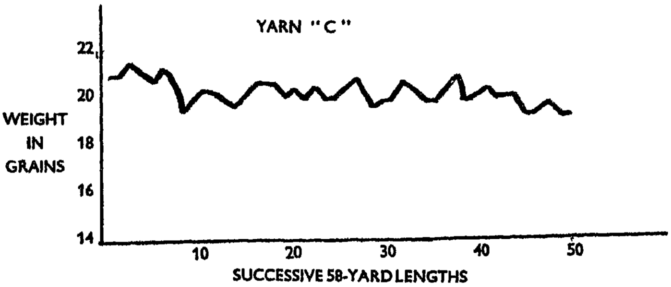

Fig 11

Uniformity of Roving

After completion of drawing the rovings produced by the three methods were compared for uniformity. This was done, as before, by cutting successive lengths and weighing them, the unit of length in this case being nine yards which weighed approximately the same as twelve inches of top. These lengths were measured with the aid of the normal one yard worsted wrap reel. After cutting, the portions of rovings were stored under constant humidity and temperature conditions before being weighed. The roving operations were effected on a 12-spindle frame, the rovings from the odd-numbered bobbins being used for testing purposes, whilst those from the even-numbered bobbins went forward for spinning. Fifty 9-yard lengths were taken from each bobbin, making a total of 300 tests for each lot, the means together with the coefficients of variation are given in Table VIII, whilst Figures 6, 7 and 8 illustrate the types of variation in the rovings from the three lots of bobbin 1.

Table VIII

Process	Mean weight of 9 yards (grains)	Coefficient of variation %
Roving A	19·2	2·0
Roving B	19·9	3·0
Roving C	19 5	4·3

Comparing the coefficients of variation together with the graphs of Figures 6, 7 and 8 for the three lots, it is evident that the regularity of the rovings has remained in the same order as in the tops, A being most uniform, followed in turn by B and C.

Uniformity of Yarns

The spun yarns, having an average count of 1/37s, were tested for long term variation in the same manner as the rovings, in this case, however, the test length was fifty-eight yards. There were two doffings, each of twelve bobbins, so the odd-numbered bobbins from the first doff were used for this test. Fifty hanks were reeled from each bobbin and the means obtained from three hundred observations. These together with the coefficients of variation are given in Table IX Figures 9, 10 and 11 illustrate the type of variation shown by the yarns from bobbin 1.

Table IX

Process	Mean weight of 58 yards (grains)	Coefficient of variation %
Yarn A	19·4	3·2
Yarn B	19·4	2 9
Yarn C	19 7	4·7

The actual means of the counts from each fifty observations obtained from the various bobbins are given in Table X to illustrate the extent of the long term count variation between bobbins and lots

Table X

Bobbin	Mean Count of 50 tests (58 yards)		
	Lot A	Lot B	Lot C
1	38·3	36·3	35·6
3	38·4	37·8	37·0
5	37 3	38 8	37·0
7	37·5	37·6	39·3
9	36·0	37·3	37·1
11	36·7	37 5	35·6
Mean	37·4	37·1	37 0

These indicate that yarn B is as uniform in count as yarn A, but yarn C is more variable.

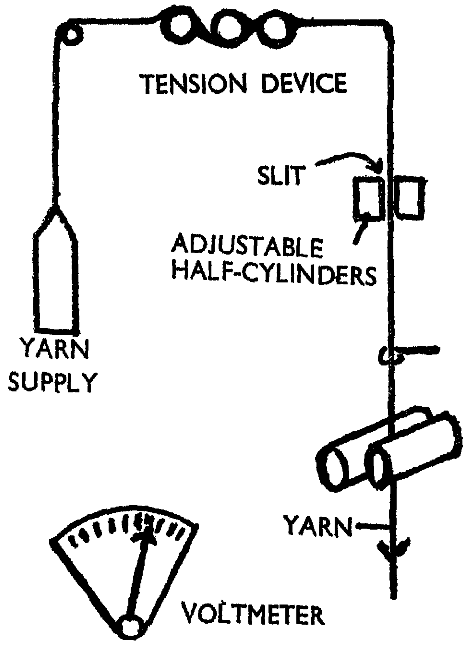

Fig 12

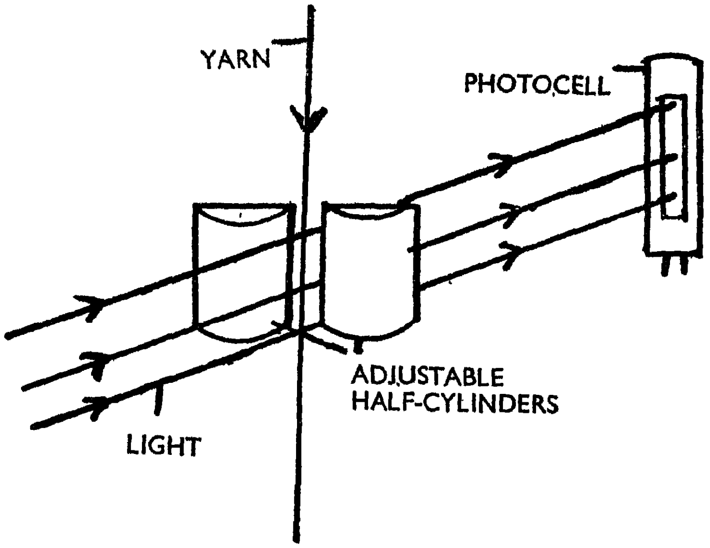

Fig. 13

Short Term Variation of Rovings and Yarns

Another investigation to determine the short term variation was carried out on the same rovings and yarns as in the previous tests The apparatus used was the general purpose photoelectric photometer devised by Chamberlain,[4] the principles of which are discussed in this *Journal*, 1944, 35, T61.

This instrument (Figures 12 and 13) can be adapted to assess the regularity of rovings and yarns. A ray of light is focussed centrally on the two adjustable half cylinders of brass, between which the yarn, suitably ten-

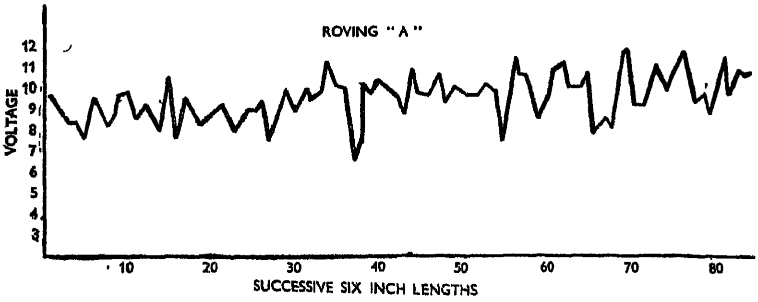

Fig. 14

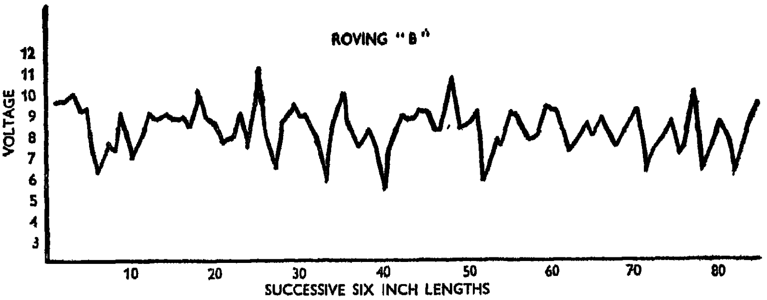

Fig. 15

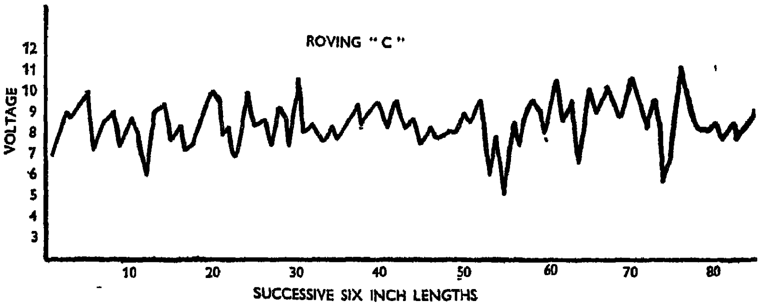

Fig. 16

sioned is passed. The light passing the yarn, through the slit, is received on a photoelectric cell whose output, suitably amplified, is recorded on a voltmeter. The slit is adjusted so that the width, without yarns, is twice that of the average diameter to be measured, and the meter reading is adjusted by means of the amplifier gain control so that when no yarn is present at the slit, the meter reads full scale (20 volts) Hence, with yarn present, the reading varies about a mean of approximately 10 volts. Two hundred observations were made along each roving and yarn, six bobbins being used in each case from the three lots A, B and C; readings being taken at six-inch intervals. The readings were grouped while being taken into 0·5 volt group intervals, and the true mean and coefficient of variation estimated from these grouped observations. The mean values and coefficients of variation so obtained are given in Table XI. The means of the voltages obtained in each case, which are arbitrary measures of the diameters together with the coefficients of variation are given in Table XI, whilst Figures 14, 15, 16 and 17, 18, 19 indicate the order of variation given by bobbin 1 of the rovings and yarns, respectively

Table XI

Lot	Roving		Yarn	
	Mean	Coefficient of variation %	Mean	Coefficient of variation %
A	8·3	15·0	8·8	21·0
B	7·6	17·2	9·5	20·2
C	7·6	18·1	9·1	21·0

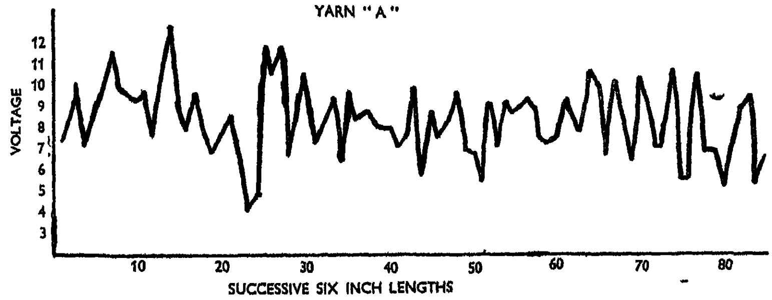

Fig 17

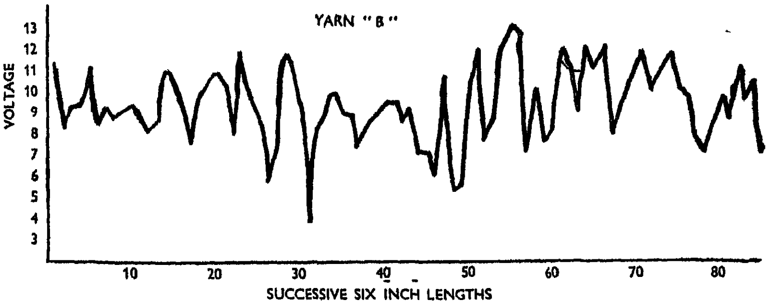

Fig. 18

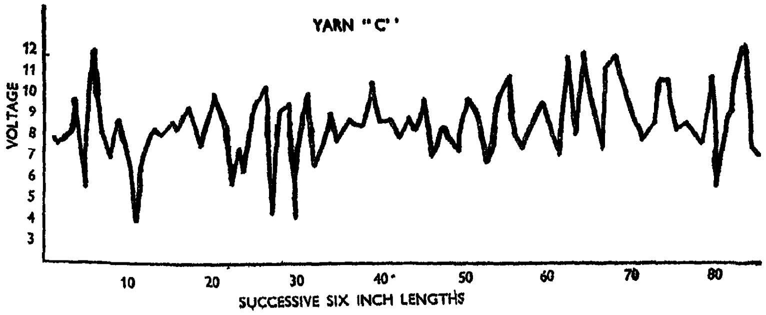

Fig 19

Comparing the coefficients of variation of the three rovings, it will be seen that A is the most uniform, followed by B and finally C. But in the case of the yarns there is very little difference in uniformity. This may be due to the fact that the spinning operation has imposed such a large degree of irregularity on the rovings that the small differences existing at the former stage are swamped by the larger irregularity due to the spinning operation. The figures relating to the yarns imply that over a short length of yarn, as generally used for visual inspection, there would be very little difference in regularity among the three lots. In practice this was found to be true, experts were unable to agree as to which yarn was the most uniform.

Yarn Strength

Finally the yarns spun on the even-numbered bobbins were tested for strength. At the same time a routine check was made to ensure that the turns per inch of the three yarns were alike. For the latter purpose twenty-five tests were made, on ten inch test pieces, at intervals down each bobbin. The strength tests were carried out on a Baër single thread machine using an 18-inch test length, under humidified conditions In all, three hundred tests were made from each lot, fifty from each of six bobbins and like the twist tests, these were spread over the whole length of the spun yarn. The results are given in Table XII.

Table XII

Lot	Turns per inch	Breaking Load (oz)	Coefficient of variation
A	15·3	3·5	14·4
B	15·6	3·5	16·1
C	15·6	3·5	16·3

Comparing the breaking loads of the three yarns it will be seen that the means are alike but the coefficients of variation indicate that yarn A is slightly more uniform This difference is, however, very small, and it is doubtful whether under industrial conditions such a small difference would be detectable

DISCUSSION

It is evident from the coefficients of variation of the three tops, given in Table VI, that these varied considerably in uniformity, A being most uniform in cross-sectional area, followed in turn by B and C. The next check on uniformity was made at the roving stage Top A, because of its greater thickness had to pass through more operations than B and C before roving, nevertheless the long term uniformity of the three rovings remained in the same order as at the top stage, A still being the most uniform. Now it is known that the irregularity of a slubbing increases as it passes through the drawing frames so that it would seem that the irregularity imposed on the more uniform top A by the whole drawing was equal to that imposed on the more irregular top, B, by the shortened drawing process and again similar to that imposed on the most irregular top, C, by the same shortened process. This same order of irregularity is also evident in the short term variations of the rovings as shown by the results in Table XI, where it will be seen that the irregularity is still in the same order.

Examination of both long and short term variations of the three yarns shows that the spinning operation has interfered with this order for B appears to be more uniform than yarn A From the point of view of long term irregularity it would seem that C is still the most irregular, the count variation as shown in Table X is fairly considerable, and such that it would not be considered a commercial yarn. From the short term irregularity examination it would appear to be equal to yarn A, but the other figures emphasise the effect of the long term variation in the roving, and it is evident that the initial one gilling operation was insufficient to reduce the irregularities of the original comb sliver On the other hand it would seem that four gillings of the comb sliver, as given to B, are sufficient to allow one to use a considerably shortened process and spin a yarn comparable with that spun from the same comb sliver which has passed through all the top finishing and drawing processes.

Comparing yarn strengths, it will be seen that these are the same for all three products, although the deviation from the mean in the case of A was least

There are two further points which must, in conclusion, be made. First, it is necessary to recognise that the count spun was 1/37s, which for a process of this nature was fairly exacting, so that irregularities in the yarns were likely to be emphasised This count was purposely chosen to exaggerate any defects which might arise from the shortened process, but it is probable that the differences between the various yarns would be less if the count spun had been lower, say, 1/12s or 1/16s Secondly, the material used in this experiment was a composite lot of wool, which had been subjected to the same scouring and carding procedures and went to the comb as one lot of wool. The combed sliver was therefore more uniform in fibre properties than would be the case in industry where the material leaving the comb at different times during the same day will have been subjected to varying scouring and carding conditions which impose other variations besides the ever present cross-sectional variation of the sliver. These will restrict the utilisation of shortened methods shown to be possible in this paper. There is also the further aspect, which has not been discussed in this paper, of the effect of shortened processes on the cost of production and the balance of machines and these would require to be considered before one departed from present-day practice Nevertheless, it has been demonstrated that given a reasonably uniform mass of wool it is possible to reduce the number of operations required to make a yarn and yet maintain the standard of product.

SUMMARY

An investigation has been made into the possibilities of utilising the sliver from a Noble comb as raw material for the drawing process. The use of such a thin sliver permits the omission of the majority of the open drawing processes. Examination of the resultant yarns shows that they compare favourably with those produced from the same wool, 64s, by the normally accepted top finishing and drawing processes, from the point of view of long and short term irregularity and yarn strength

ACKNOWLEDGEMENT

The authors wish to thank Messrs. T F Griffin and R. H. Heddon for assistance in the processing of the wool, Dr N H. Chamberlain for assistance in the measurement of the short term irregularities, and the International Wool Secretariat for grants which made this work possible

REFERENCES

[1] Martindale, J G *J Text Inst*, 1942, 33, P9.
[2] McConnel, R J *Textile World*, 1947, 97, No 3, 110
[3] Daniels, H. E. *J Text. Inst.*, 1942, 33, T137.
[4] Chamberlain, N H *J. Text. Inst*, 1944, 35, T61

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Received 16/2/49

Letters to the Editor

To the Editor, *Journal of the Textile Institute.*

A BALLISTIC METHOD FOR THE DETERMINATION OF INTER-PLY ADHESION

In the above paper, the author states that for adhesive tape the points on the graph of Area Peeled-Work are more dispersed than for other systems This touches the fringe of the matter, and considerable war-time experience with adhesive tapes suggests that a satisfactory test-method simply does not exist, despite numerous efforts

A particular warning seems desirable, in a large-scale investigation it was found that various forms of "rate-of-peeling" test (using aluminium, plate glass, *etc.*) and American-type tests (maximum load to strip at a steady rate), all placed a series of commercial adhesive tapes in the same order, which agreed roughly with practical evaluations. The ballistic test, however, placed them in almost the inverse order.

This behaviour is dependent on the physical properties of the adhesive mass, and different makes behave in different ways, even on qualitative test. One will withstand a small steady pull well, but will strip easily with a sudden jerk; another will withstand a sudden jerk, but will peel off easily under a small steady load. Cases occur where material behaving very poorly on a stripping test behaves perfectly well in practical use.

The purpose of this letter is therefore twofold, first to draw attention to the danger of accepting a ballistic test without much comparative testing, and secondly, to point out that the field of research on testing "adhesion" of masses having various degrees of thixotropy, viscosity, true elasticity, rubbery "tack", and other vague physical properties, is still wide open to anyone who will bring the necessary skill and time to it.

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James Hardcastle & Co Ltd ,
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THE JOURNAL OF THE
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TRANSACTIONS

40—THE EFFECTS OF SODIUM CHLORIDE, PYRIDINE AND ETHYL ALCOHOL ON THE ABSORPTION SPECTRA OF CERTAIN AZO DYES IN AQUEOUS SOLUTION

By J. T. MARTIN and H. A. STANDING

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ABSTRACT

Sodium chloride has a considerable effect upon the absorption spectra of solutions of Benzopurpurine 4B, its meta isomer and Direct Fast Orange SE in water. These dyes are known from other evidence to form aggregates in the solution when sodium chloride is added to it. The spectra of Chrysophenine G and Naphthalene Orange 2G in aqueous solution are unaffected by the addition of salt; it is known that these dyes are not appreciably aggregated by salt. The spectral effect of sodium chloride is therefore probably due to aggregation of the dye.

When dissolved in aqueous pyridine containing 10 per cent or more of pyridine, none of the dyes shows any considerable change in its absorption spectrum on the addition of sodium chloride to the solution. The presence of pyridine in the dye solution therefore probably prevents the aggregation of the dye by the salt. The spectrum of each dye in aqueous pyridine depends upon the percentage of pyridine in the solution, but even when the pyridine concentration is only 10 per cent., the spectrum of the dye differs significantly from that of the dye in water.

The absorption spectrum of each dye in aqueous ethyl alcohol is independent of the concentration of sodium chloride in the solution when the alcohol concentration is 50 per cent. but not when it is 10 per cent The spectrum of each dye in aqueous alcohol (free from salt) depends on the percentage of alcohol in the solution, the effect of 10 per cent. alcohol on the spectrum of the dye is small, however, compared with the effect of 10 per cent pyridine It is suggested that the spectral effect of ethyl alcohol is due to the effect of alcohol on the dielectric constant of the solution whereas the spectral effect of pyridine is due in part to complex formation between the pyridine and the dye

INTRODUCTION

During investigations of the absorption of direct dyes by cellulose, the concentration of dye solutions is estimated colorimetically. These solutions may contain inorganic electrolytes, such as sodium chloride, in addition to the dye, and they may also contain non-electrolytes, such as pyridine, that have been used for the extraction of the dye from the dyed material. It is well recognised that the presence of such compounds in aqueous dye solutions may have considerable effect on the absorption spectrum of the dye, and a preliminary investigation of these effects is usually necessary for the colorimetric analysis of the dye solutions. Observations originally made in this connection led to the work described in this paper.

The inorganic electrolyte used was sodium chloride, the non-electrolytes were pyridine and ethyl alcohol. Pyridine is frequently used for extracting dyes from dyed cellulose, and ethyl alcohol was included in the investigation to see whether the spectral effects of pyridine were typical of a non-electrolyte.

The dyes were: the dis-azo direct dyes, Benzopurpurine 4B (Colour Index 448), Direct Fast Orange SE (Colour Index 326), Chrysophenine G (Colour Index 365), the dis-azo dye meta-Benzopurpurine 4B isomeric with Benzopurpurine 4B but of relatively low substantivity towards cellulose; and the mono-azo wool dye Naphthalene Orange 2G (Colour Index 151). These particular dyes were chosen chiefly because they had already been purified for other work.

1. THE SPECTRAL EFFECT OF SODIUM CHLORIDE

When the dye concentration is maintained constant the absorption spectrum of Benzopurpurine 4B in aqueous solution depends upon the concentration of sodium chloride present in the solution As the sodium chloride concentration is increased the maximum extinction coefficient of the dye decreases, and the spectral peak is displaced slightly towards the violet This effect is shown in Fig. 1 for dye solutions which were measured

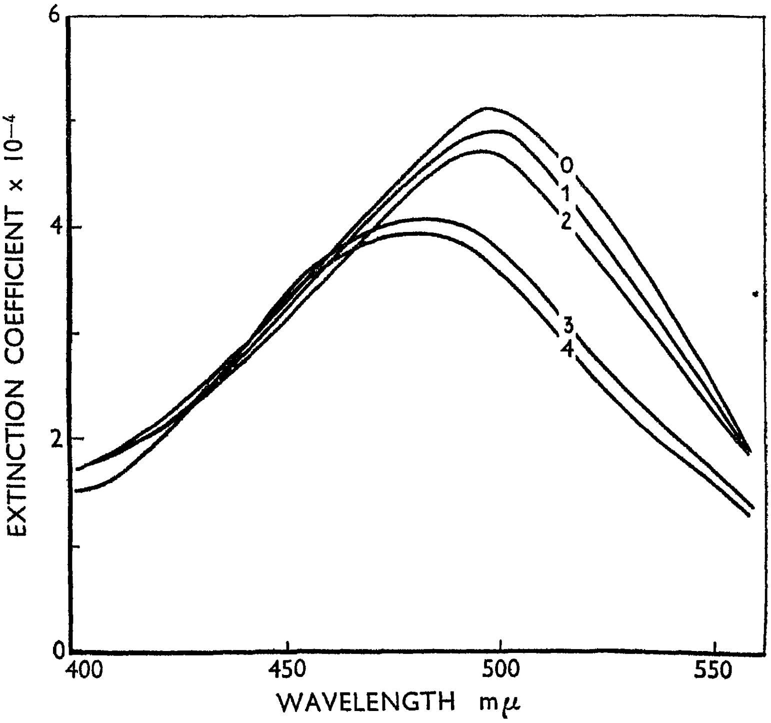

Fig. 1. Absorption Spectra of Benzopurpurine 4B in Aqueous Solution containing Sodium Chloride

Dye 10 mg /l NaCl concentration (g /l) shown on each curve

6 days after their preparation, the dye concentration being maintained constant at 10 mg./l. and the salt concentration (shown on each curve) being varied from 0 to 4 g. per litre. The figure also shows that although the extinction coefficients at the peak and the longer wavelengths vary considerably with the salt concentration, those at the shorter wavelengths do not vary appreciably

The effect of sodium chloride on the absorption spectrum of each of the other azo dyes is shown in Figs 2a—d, the concentration of the dye is maintained constant and the sodium chloride concentration is varied The spectra of meta-Benzopurpurine 4B (Fig 2a) and of Direct Fast Orange SE (Fig. 2b) depend upon the concentration of sodium chloride in the aqueous dye solution As the salt concentration is increased the maximum extinction coefficient of the dye decreases, and the spectral peak is displaced slightly towards the violet for meta-Benzopurpurine 4B and towards the red for Direct Fast Orange SE. On the other hand the spectra of Chrysophenine

Fig. 2. Absorption Spectra of the Dyes in Aqueous Solution containing Sodium Chloride.

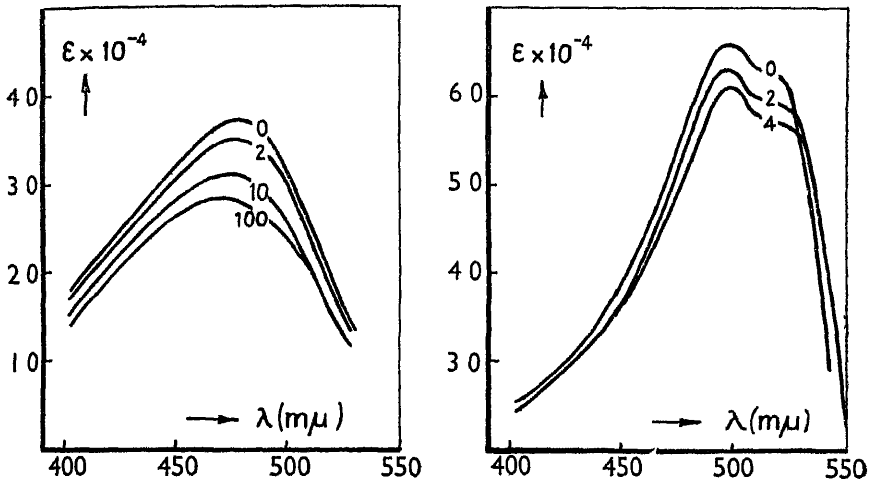

Fig 2a. Meta-Benzopurpurine 4B
Dye concentration 10 mg./l.
Sodium chloride concentration (g./l.)
shown on each curve

Fig 2b. Direct Fast Orange SE.
Dye concentration 7·5 mg./l.
Sodium chloride concentration (g./l.)
shown on each curve.

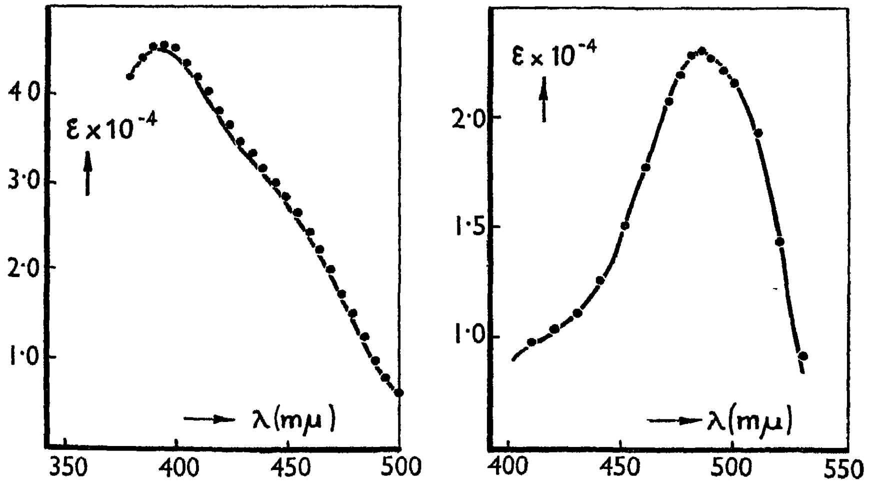

Fig. 2c. Chrysophenine G.
Dye concentration 10 mg./l
———— No sodium chloride.
. . . . . 4 g. sodium chloride per l.

Fig 2d Naphthalene Orange 2G.
Dye concentration 10 mg /l
———— No sodium chloride
. . . . . 4 g. sodium chloride per l.

G (Fig. 2c) and of Naphthalene Orange 2G (Fig 2d) are practically independent of the concentration of sodium chloride in the aqueous dye solution.

At 25°C. Chrysophenine G and Naphthalene Orange 2G are almost molecularly dispersed[1,2] in aqueous solution containing sodium chloride, the other three dyes, however, are considerably aggregated[1,2,3] by sodium chloride in aqueous solution. The spectral effect of sodium chloride is therefore probably due to the aggregation of the dye by the salt.

The absorption spectra of Benzopurpurine 4B solutions containing not more than 2 g. sodium chloride per litre do not alter appreciably during the six days following the preparation of the solutions. When the salt concentration is 3 or 4 g. per litre, however, the absorption spectrum of the solution alters considerably during the first 24 hours after preparation and slightly during the succeeding week. This effect may be due to a slow attainment of the final state of aggregation. No significant alteration of the spectrum with time occurs with Direct Fast Orange SE solutions, and only small changes occur with meta-Benzopurpurine 4B solutions.

2. THE SPECTRAL EFFECT OF PYRIDINE

Aqueous pyridine solutions are frequently used to extract dyes from dyed cellulose; they have also been used for the colorimetric analysis of mixtures of direct dyes. Thus Neale and Stringfellow[4] observed that the spectra of two direct dyes in 25 per cent. aqueous pyridine* were almost additive whereas the spectra of the same dyes in water were not. They suggested that in aqueous solution one direct dye can form a complex with another, and that the presence of pyridine in the aqueous dye solution prevented any such complex formation It therefore seemed probable that the presence of pyridine in an aqueous dye solution might also prevent the aggregation of the dye by sodium chloride; and the effect of sodium chloride upon the absorption spectra of the dyes in aqueous pyridine was therefore investigated. This investigation was confined to the three dyes, Benzopurpurine 4B, meta-Benzopurpurine 4B and Direct Fast Orange SE since sodium chloride has no effect upon the spectra of the other two dyes in water.

At 25° C. Benzopurpurine 4B is precipitated from an aqueous 10 mg./l. solution by the addition of about 6 g. sodium chloride per litre. When the dye is dissolved in 25 per cent. aqueous pyridine, however, it remains in solution even when 50 g. sodium chloride per litre is added. A similar effect is observed with Direct Fast Orange SE. The effect of sodium chloride on the absorption spectra of these dyes in 25 per cent. aqueous pyridine can therefore be investigated over a much wider range of salt concentration than is possible for solutions of the dyes in water alone

The absorption spectrum of Benzopurpurine 4B (10 mg./l.) in 25 per cent. aqueous pyridine is practically independent of the concentration (0 to 50 g./l.) of sodium chloride present in the solution This is shown by the following values of the maximum molar extinction coefficients (ε_{max}).

Sodium chloride (g /l.)	0	4	10	50
$\varepsilon_{max} \times 10^{-4}$	5 44	5 46	5 46	5 49

The absorption spectra of these solutions are practically independent of the age of the solutions during the week following their preparation. The absorption spectra of meta-Benzopurpurine 4B and Direct Fast Orange SE in 25 per cent aqueous pyridine are also practically independent of the sodium chloride concentration (0 to 50 g./l.). These results therefore lead to the conclusion that when the aqueous dye solution contains 25 per cent. of pyridine, the dye is not aggregated by sodium chloride.

The effect of sodium chloride on the absorption spectrum of Benzopurpurine 4B (10 mg./l.) in aqueous pyridine solutions containing only 5 per cent and 10 per cent. pyridine by volume was also investigated. When the pyridine concentration is 10 per cent. the dye is not precipitated from solution by the addition of 50 g. sodium chloride per litre, and the absorption spectrum of the dye in 10 per cent aqueous pyridine is almost independent of the concentration (0 to 50 g./l) of sodium chloride in the solution. When the pyridine concentration is only 5 per cent , the dye is precipitated from the solution by 50 g. sodium chloride per litre but not by 10 g. salt per litre. The absorption spectrum of the dye in 5 per cent aqueous pyridine depends on the concentration (0 to 10 g /l.) of sodium chloride in the solution, the maximum extinction coefficient of the dye decreasing with increasing salt concentration. However, the decrease is very much smaller than that for solutions without pyridine, as shown by the values of the maximum extinction coefficients in the following table.

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*In the paper the phrase " 25 per cent. aqueous pyridine" is used to describe a pyridine-water mixture containing 25 per cent by volume of pyridine. The phrase " 25 per cent aqueous alcohol" is used in a similar sense.

Sodium chloride (g /l)		0	2	4	10
Benzopurpurine 4B in water ...	$\varepsilon_{max} \times 10^{-4}$	5·12	4·75	4·07	dye precipitated
Benzopurpurine 4B in 5% aq. pyridine	$\varepsilon_{max} \times 10^{-4}$	5·25	5·15	5·07	5·02

Thus even when the concentration of pyridine in the aqueous dye solution is only 5 per cent., the spectral effect of sodium chloride is considerably reduced.

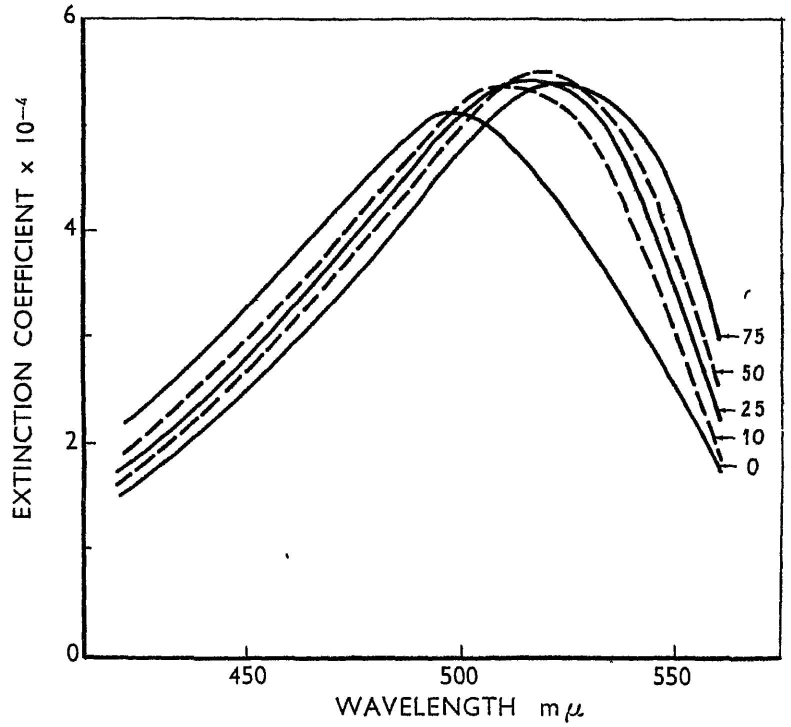

Fig 3. Absorption Spectra of Benzopurpurine 4B in Pyridine-Water Mixtures. Dye 10 mg /l % Pyridine (by volume) in solution shown on each spectrum

Although no new absorption bands are developed, the absorption spectrum of Benzopurpurine 4B in aqueous pyridine (free from sodium chloride) differs significantly from that of the dye in water alone. Fig 3 shows that the spectrum of the dye (10 mg /l) in aqueous pyridine depends on the percentage of pyridine in the solution. As the pyridine concentration is increased, the maximum extinction coefficient of the dye increases (up to 50 per cent. pyridine), and the entire spectrum is progressively displaced towards the red. The displacement is considerable even when the pyridine concentration is only 10 per cent; moreover the displacement when the pyridine concentration is increased from 0 to 25 per cent. is greater than

Fig. 4. Absorption Spectra of the Dyes in Water and in Aqueous Pyridine. Percentage by volume of pyridine in solution shown on each curve.

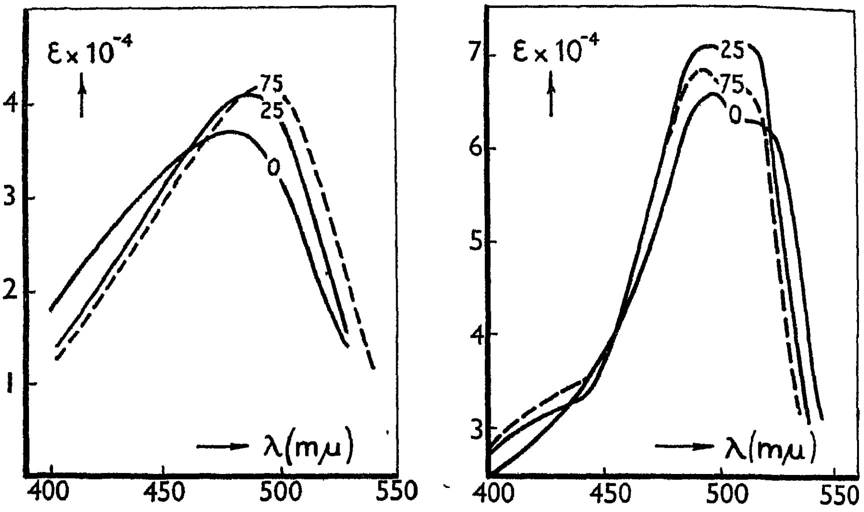

Fig. 4a. Meta-Benzopurpurine 4B. (10 mg /l)

Fig 4b. Direct Fast Orange SE (7·5 mg /l.)

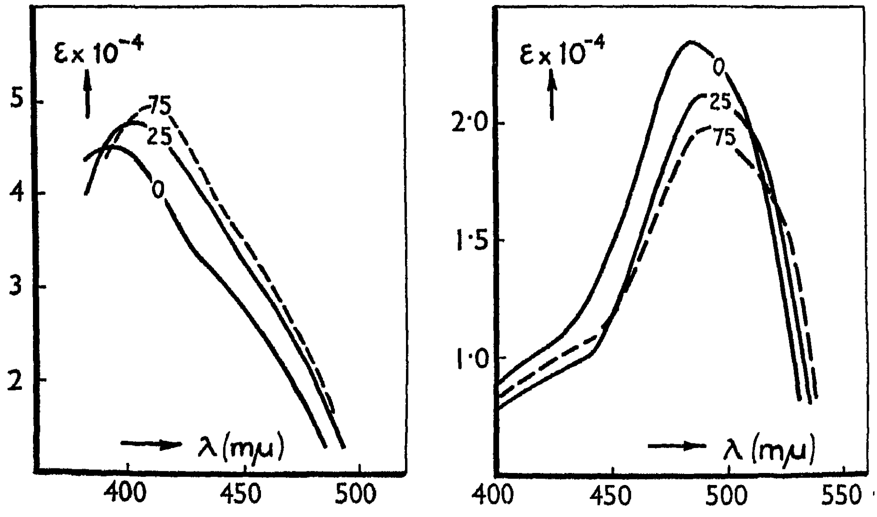

Fig 4c Chrysophenine G (10 mg /l)

Fig. 4d. Naphthalene Orange 2G (10 mg /l)

the displacement corresponding to an increase in the pyridine concentration from 25 to 75 per cent.

Fig. 4 shows the spectrum of each of the other dyes in water, 25 per cent aqueous pyridine and in 75 per cent aqueous pyridine. The entire spectrum of each dye is considerably displaced by the presence of 25 per cent. pyridine in the aqueous dye solution, the displacement is towards the violet for Direct Fast Orange SE (Fig 4b) and towards the red for the other three dyes. Although the spectrum is progressively displaced as the pyridine concentration is increased, the displacement for an increase from 0 to 25 per cent. pyridine is greater than that for an increase from 25 to 75 per cent. pyridine.

Thus for each of the dyes the addition of 25 per cent pyridine to the aqueous dye solution has a relatively large effect upon the spectrum of the dye.

The results show that when the dye solution contains 25 per cent. pyridine, the absorption spectrum of the dye is not only independent of the concentration of sodium chloride in the solution, but is also significantly different from that of the dye in water alone. These facts can be explained by the hypothesis that pyridine forms a complex with the dye, that the pyridine-dye complex is not aggregated by sodium chloride, and that its spectrum differs from that of the dye An alternative hypothesis is that the effects of pyridine are due to the fact that the dielectric constant of pyridine is considerably lower than that of water—the smaller the dielectric constant of the solvent, the greater is the electrostatic repulsion between two dye anions, and in consequence the smaller the aggregation of the dye. This same hypothesis could account for the effect of pyridine on the absorption spectrum of the dye since it is generally believed that the absorption spectrum of a solute depends on the dielectric constant of the solvent

Whereas the hypothesis of complex formation demands a specific interaction between certain groups of the dye molecule and the pyridine, the second hypothesis implies that any solvent whose dielectric constant is much less than that of water will have an effect similar to that of pyridine on the absorption spectrum of the dye. The effect of another solvent, namely, ethyl alcohol, was therefore investigated. This investigation, which is described in the following section, was concerned with: (1) the effect of sodium chloride on the spectrum of the dye in aqueous alcohol and (2) the effect of alcohol upon the spectrum of the dye in salt-free aqueous solution.

3. THE SPECTRAL EFFECT OF ETHYL ALCOHOL

The object of these experiments was to see whether the presence of ethyl alcohol in the aqueous dye solution prevented the aggregation of the dye by sodium chloride. Since aggregation may not be complete within an hour of the preparation of the solutions, it is desirable to measure the spectra of the solutions after longer intervals The absorption spectrum of Benzopurpurine 4B in aqueous ethyl alcohol depends, however, on the age of the solution even when the solution is free from salt; as the age increases the maximum extinction coefficient of the dye decreases This behaviour, which is not understood, may be due to decomposition of the dye by alcohol since the decrease in the extinction coefficient when the solution is left to stand is very large under certain conditions. A slow change with time was also observed in the spectra of salt-free solutions of meta-Benzopurpurine 4B containing alcohol, but not in solutions of Direct Fast Orange SE. Further details of the behaviour are given in the experimental section. It is sufficient to say here that, owing to this effect, it was difficult to decide whether any aggregation of the dye in aqueous alcohol solutions containing sodium chloride was complete within an hour The spectra described in this section were all measured within an hour of the preparation of the solutions, and the conclusions are therefore only established for freshly prepared solutions.

When Benzopurpurine 4B is dissolved in 50 per cent aqueous ethyl alcohol, it is not precipitated from solution by the addition of sodium chloride of relatively high concentration. Thus whereas the dye is precipitated from an aqueous 10 mg /l. solution by the addition of about 6 g. sodium chloride per litre, it is not precipitated from a 50 per cent. aqueous alcohol solution by 50 g salt per litre. Direct Fast Orange SE behaves similarly. Ethyl alcohol has therefore the same effect as pyridine—it prevents the precipitation of the dye from solution by sodium chloride of relatively high concentration.

When, however, the percentage by volume of ethyl alcohol in a 10 mg./l Benzopurpurine 4B solution is only 10 per cent., the dye is precipitated from solution by the addition of 10 g sodium chloride per litre. This contrasts with the effect of pyridine previously described, namely, Benzopurpurine 4B (10 mg./l) is neither precipitated from a 10 per cent aqueous pyridine solution by the addition of 50 g. salt per litre, nor is it precipitated from a 5 per cent. aqueous pyridine solution by 10 g. salt per litre. The contrast would evidently be still greater if concentrations were expressed in molarities. Thus low concentrations of ethyl alcohol are not so effective as low concentrations of pyridine in preventing the precipitation of the dye from solution by sodium chloride

The absorption spectrum of Benzopurpurine 4B (10 mg./l) in 50 per cent. aqueous alcohol is practically independent of the concentration (0 to 50 g./l.) of sodium chloride in solution. Meta-Benzopurpurine 4B and Direct Fast Orange SE behave similarly. On the other hand, the spectrum of Benzopurpurine 4B (10 mg./l.) in 10 per cent. aqueous alcohol depends on the concentration of sodium chloride in the solution; as the salt concentration increases the maximum extinction coefficient of the dye decreases as shown in the following table.

Sodium chloride (g /l)	0	2	4	10
$\varepsilon_{max} \times 10^{-4}$	5·28	5·01	4·83	dye precipitated

Thus although sodium chloride has no effect upon the absorption spectrum of the dye in 50 per cent. aqueous alcohol, it has a significant effect upon the spectrum of the dye in 10 per cent aqueous alcohol. In contrast, the presence of 10 per cent pyridine in the dye solution eliminates the spectral effect of salt over a wide range of concentration (0 to 50 g /l)

Ethyl alcohol has a significant effect upon the absorption spectrum of Benzopurpurine 4B in salt-free solution Fig. 5 shows that when the dye concentration is maintained constant, the spectrum of Benzopurpurine 4B (10 mg /l.) in aqueous alcohol depends on the percentage of alcohol in the solution. As the alcohol concentration increases the maximum extinction coefficient of the dye increases. Although the extinction coefficients at the peak and the longer wavelengths vary considerably with the alcohol concentration, those at the shorter wavelengths do not vary appreciably. Thus in contrast to pyridine ethyl alcohol does not displace the entire spectrum of the dye.

Fig. 5 also shows the absorption spectra—reproduced from Fig 1—of Benzopurpurine 4B in aqueous solution containing sodium chloride. The effect of sodium chloride (as of ethyl alcohol) on the absorption spectrum of the dye is greatest at the peak and the longer wavelengths. On the other hand whereas the spectral effect of ethyl alcohol is to raise the peak and to displace it towards the red, the effect of sodium chloride is to depress the peak and to displace it towards the violet The spectral effect of ethyl alcohol is therefore similar in kind, though opposite in direction, to that of sodium chloride, the two sets of curves have the appearance of belonging to one family.

The effects of ethyl alcohol on the absorption spectra of meta-Benzopurpurine 4B and of Direct Fast Orange SE are similarly related to those of sodium chloride. As shown in Fig. 6a the spectral effect of ethyl alcohol is to raise almost the entire spectrum of meta-Benzopurpurine 4B whereas the effect of sodium chloride is to depress the entire spectrum. Similarly as shown in Fig 6b the spectrum of Direct Fast Orange SE is raised and displaced towards the violet by alcohol whereas it is depressed and displaced towards the red by salt.

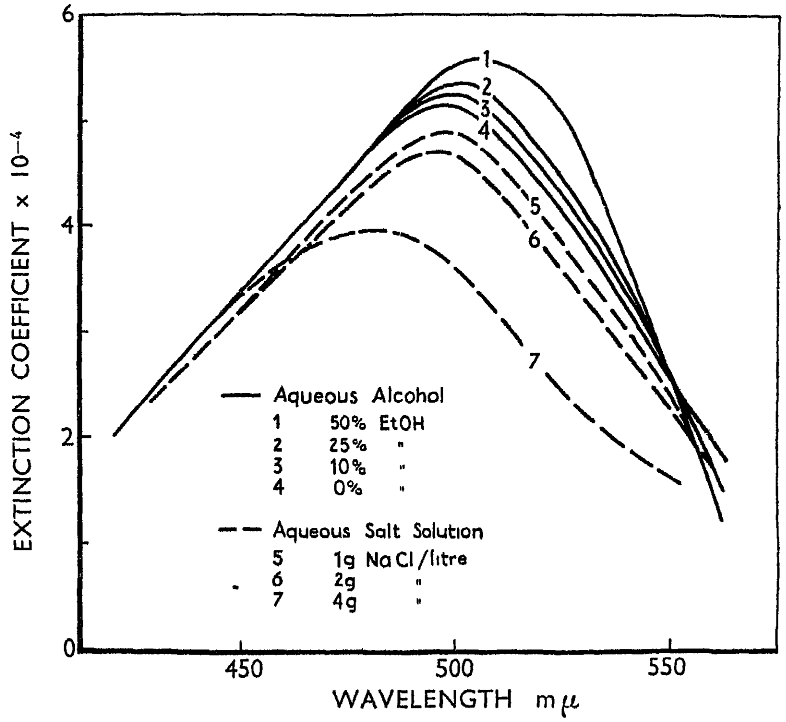

Fig 5 Absorption Spectra of Benzopurpurine 4B in Water and in Aqueous Alcohol. Continuous curves—spectra of the dye in aqueous alcohol Dotted curves—spectra of the dye in aqueous salt solution

Ethyl alcohol, however, has an effect not only on the spectra of these three dyes which are aggregated by salt but also on the spectra of Chrysophenine G and Naphthalene Orange 2G, neither of which is appreciably aggregated by salt. Thus Fig. 6c shows that the maximum extinction coefficient of Chrysophenine G in aqueous alcohol increases as the alcohol concentration is increased from 0 to 70 per cent.; the spectrum is not, however, displaced as much towards the red by alcohol as by pyridine Fig. 6d shows that the maximum extinction coefficient of Naphthalene Orange 2G in aqueous alcohol decreases with increasing alcohol concentration The effect of 25 per cent alcohol upon the absorption spectrum of the dye is, however, much less than that of 25 per cent. pyridine, the maximum extinction coefficient of the dye is not decreased as much by the alcohol as by the pyridine, nor is the spectrum displaced as much towards the red

These results show that ethyl alcohol has an effect upon the spectrum of each of the dyes. The effect, however, is smaller than, and different from, that of pyridine. The principal effect of alcohol is to alter the maximum extinction coefficient of the dye whereas that of pyridine is to displace the entire spectrum towards either the red or the violet.

Fig. 6. Absorption Spectra of the Dyes in Aqueous Alcohol. Percentage by volume of alcohol in solution shown on each curve.

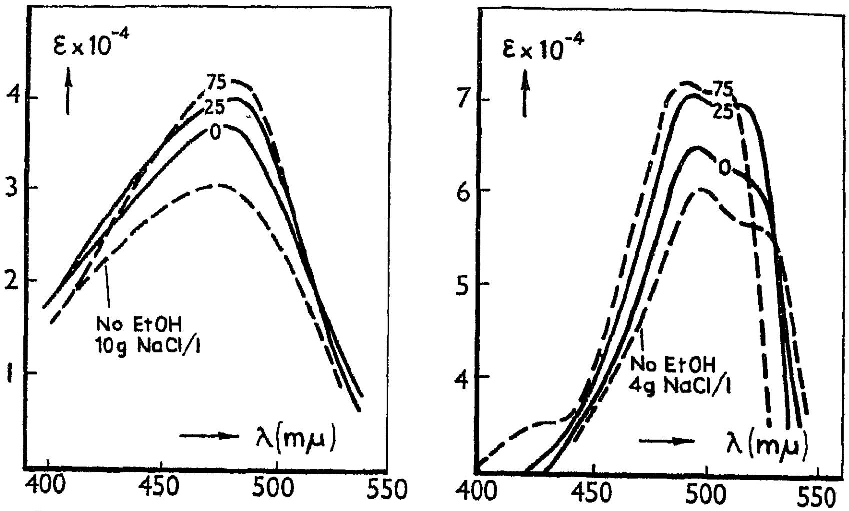

Fig. 6a. Meta-Benzopurpurine 4B. (10 mg./l.)

Fig. 6b. Direct Fast Orange SE (7·5 mg./l.)

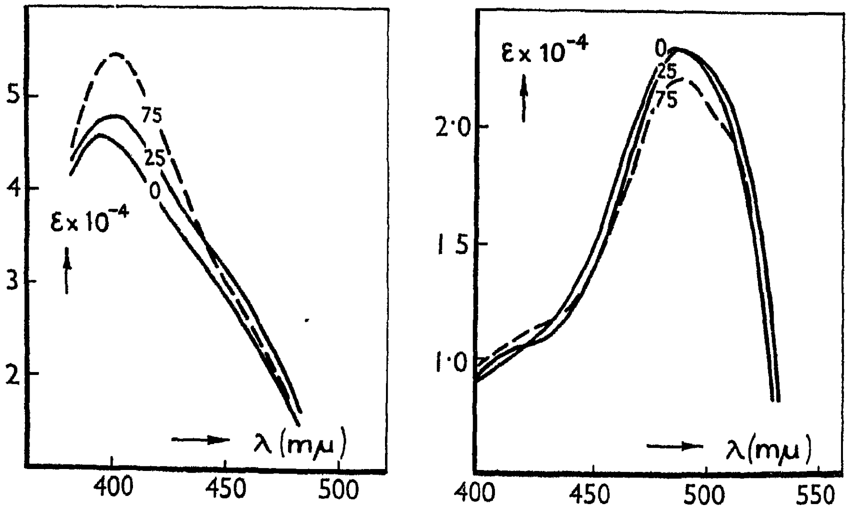

Fig. 6c. Chrysophenine G. (10 mg./l.)

Fig. 6d. Naphthalene Orange 2G (10 mg./l.)

DISCUSSION

It has been shown that sodium chloride has a significant effect upon the absorption spectra of those dyes which are aggregated in aqueous salt solution, and that it has no appreciable effect upon the spectra of the dyes which are not aggregated by salt. These results lead to the conclusion that the spectral effect of sodium chloride is due to the aggregation of the dye by the salt. In this respect it is interesting to note that Sheppard and Geddes[5] have observed deviations from Beer's Law for salt-free aqueous solutions of Benzopurpurine 4B and meta-Benzopurpurine 4B. They found that as the dye concentration was increased, the maximum extinction coefficient of each dye decreased and the spectral peak was displaced slightly towards the violet. They attributed this effect to an increase in the degree of aggregation of the dye with increasing dye concentration. The similarity between these spectral changes in salt-free solutions and those that occur when sodium chloride is added to the aqueous dye solution supports the conclusion that the spectral changes are due to the aggregation of the dye.

The fact that the absorption spectrum of the dye depends upon the sodium chloride concentration leads to the conclusion that the degree of aggregation increases steadily with increasing salt concentration. Aqueous diffusion measurements[1,2] have suggested that this is so for Benzopurpurine 4B and Direct Fast Orange SE. The alteration with time of the spectrum of Benzopurpurine 4B in aqueous solution containing 3 g. or 4 g. sodium chloride per litre may be due to a slow attainment of the final state of aggregation; other workers[6] have concluded that the degree of aggregation of some dyes in salt solutions varies with the age of the solution. On the other hand, although no precipitation of dye from the solutions was observed during the six days following their preparation, the solutions may have been supersaturated. As shown in Fig. 1 the effect of increasing the sodium chloride concentration from 2 g. to 3 g per litre is relatively large.

The fact that the absorption spectra of the dyes in aqueous pyridine are independent of the concentration of sodium chloride in the solution leads to the conclusion that in the presence of pyridine the dyes are not aggregated by salt. As previously stated this effect may be due to one of two causes: (1) complex formation between the dye and the pyridine and (2) the decrease in the dielectric constant of the solution. The effect of ethyl alcohol was studied to distinguish between these two hypotheses.

The dielectric constant of water is 80, that of ethyl alcohol 25 and that of pyridine 12·4. Wyman[7] has shown that the dielectric constant of alcohol-water mixtures decreases almost linearly as the percentage of alcohol by volume is increased; thus the dielectric constant of 10 per cent. aqueous alcohol is only about 6 per cent. lower than that of water. The variation of the dielectric constant of pyridine-water mixtures with the pyridine concentration is not known, but the dielectric constant of 10 per cent. aqueous pyridine is probably not much lower than that of 10 per cent. aqueous alcohol.

It has been shown that the absorption spectrum of Benzopurpurine 4B in aqueous alcohol is independent of the salt concentration when the alcohol concentration is 50 per cent. but not when it is 10 per cent. This effect can probably be attributed to the change in the dielectric constant of the solution. On the other hand the absorption spectrum of the dye in 10 per cent. aqueous pyridine is independent of the salt concentration and moreover the spectrum of the dye in 5 per cent. aqueous pyridine depends only slightly on the salt concentration It seems improbable that the dielectric constant of the solution is lowered sufficiently by the presence of 5 or 10 per cent. pyridine to almost prevent the aggregation of the dye by the salt.

Pyridine is not only more effective than alcohol in preventing the aggregation of the dye by sodium chloride but it also has a greater effect than alcohol upon the absorption spectrum of the dye. This is shown in Fig. 7 where the wave-length λ_{max} of maximum absorption of each dye is plotted against the percentage by volume of alcohol or pyridine in the dye

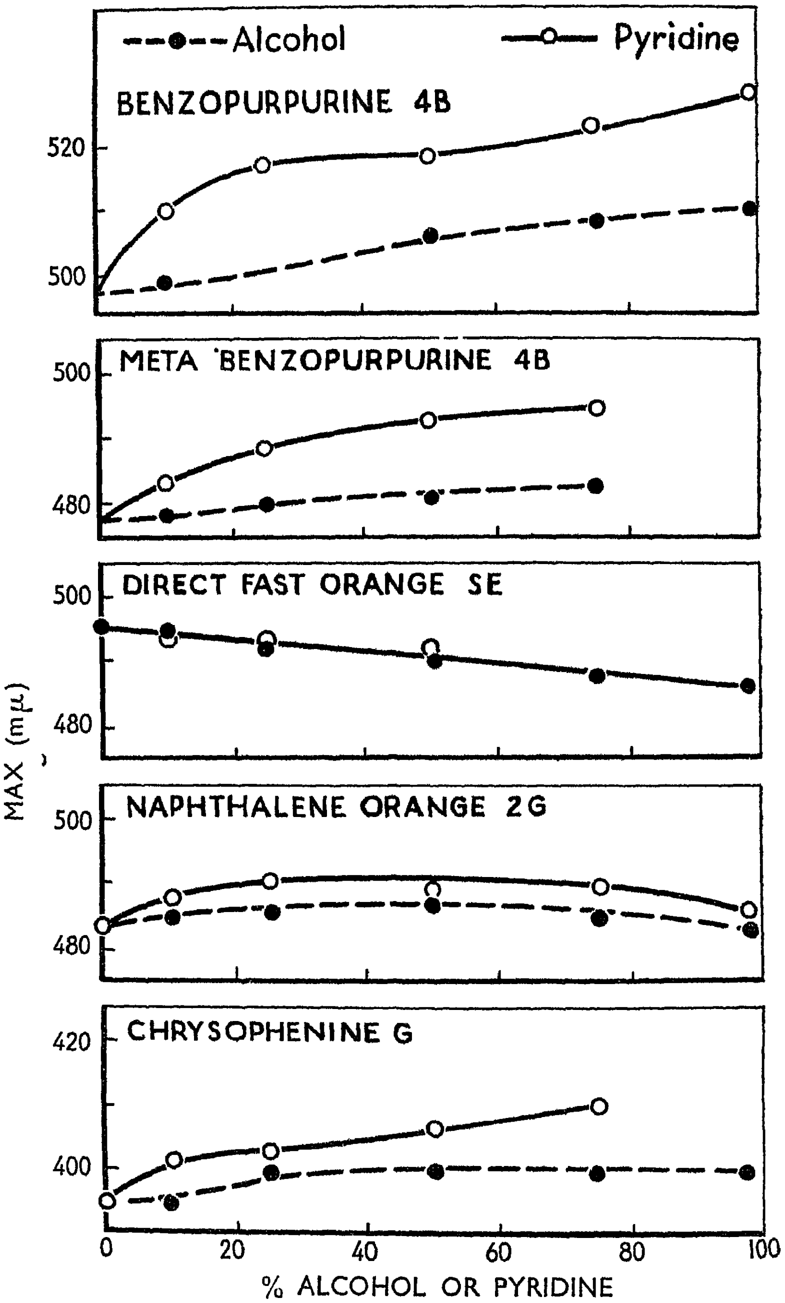

Fig 7. Dependence of λ_{max} on the Composition of the Solution.

Fig. 8.—Absorption Spectra of the Dyes in Water. 10% Aqueous Alcohol and 10% Aqueous Pyridine.

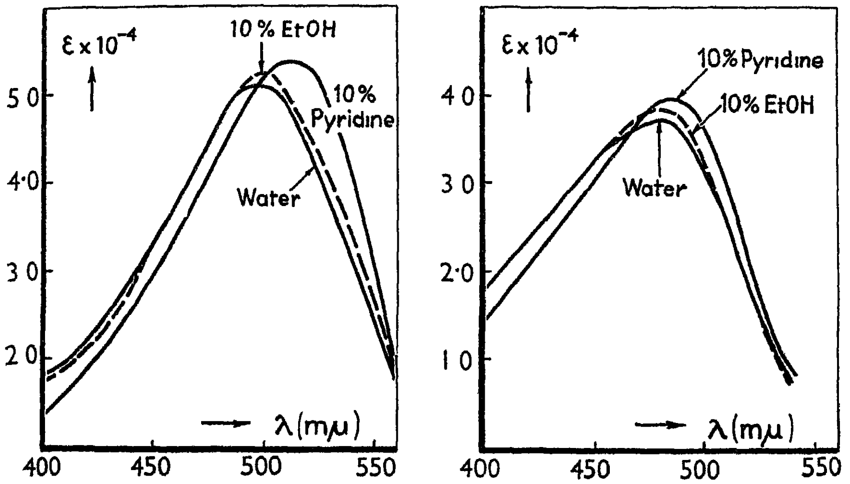

Fig 8a Benzopurpurine 4B. (10 mg /l.)

Fig. 8b Meta-Benzopurpurine 4B. (10 mg /l)

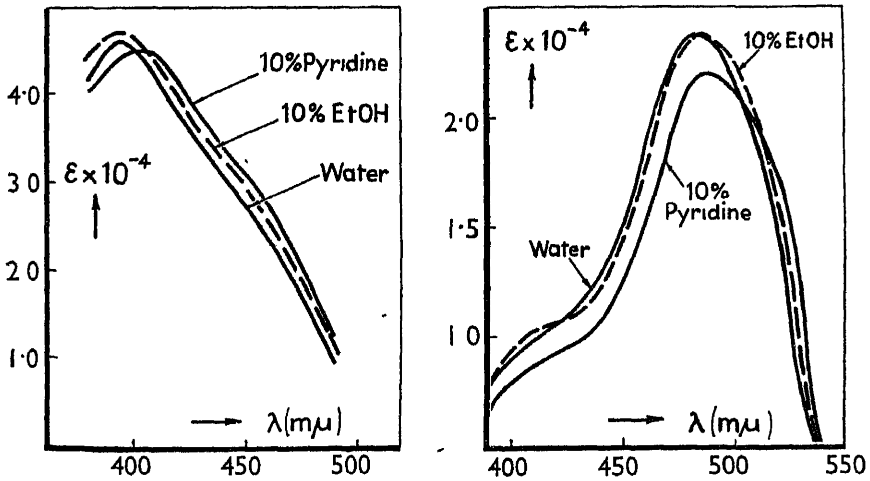

Fig. 8c. Chrysophenine G. (10 mg /l)

Fig 8d Naphthalene Orange 2G. (10 mg /l)

solution. With the exception of Direct Fast Orange SE* the wave-length of maximum absorption of each dye is displaced much more by the pyridine than by the alcohol over the entire concentration range. Thus the presence of 25 per cent. pyridine in the aqueous dye solution displaces λ_{max} more than does the presence of 90 per cent. alcohol. Moreover whereas λ_{max} varies fairly steadily with the alcohol concentration, it increases more rapidly with low pyridine concentrations (0-10 per cent.) than it does with high concentrations of pyridine.

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*The spectral behaviour of Direct Fast Orange SE is in many ways different from that of the other dyes. The spectrum of the dye in water (Fig. 2b) has two peaks, a fairly sharp one at about 495 mμ and a subsidiary peak—not very well defined—at about 520 mμ. The addition of 25 per cent pyridine to the aqueous solution not only displaces the spectrum towards the violet (Fig 4b), but also alters its shape; the subsidiary peak is developed and becomes as pronounced as the other peak

The difference, most marked at low concentrations, between the spectral effects of pyridine and alcohol is also shown in Fig 8. This shows that the spectrum of each dye in 10 per cent aqueous alcohol is not greatly different from that of the dye in water. The presence of 10 per cent. pyridine in the aqueous dye solution, however, has a significant effect on the spectrum of each dye, the entire spectrum being displaced towards the red.

The fairly regular variation of λ_{max} with increasing alcohol concentration and the small spectral effect of 10 per cent. alcohol can probably be attributed to a lowering of the dielectric constant of the solution by the alcohol. The way in which the change in the dielectric constant of the solution affects the spectrum of the dye is not known. The fact that the spectral effect of alcohol is opposite to that of salt would suggest that the dye is slightly aggregated in salt-free aqueous solution and becomes less aggregated as the dielectric constant of the solution is lowered by the addition of alcohol. It is improbable, however, that the spectral effect of alcohol can be entirely attributed to a disaggregation of the dye since alcohol has also an effect upon the spectra of Chrysophenine G and Naphthalene Orange 2G, each of which is almost molecularly dispersed in aqueous solution.

The significant difference between the spectral effects of low concentrations of pyridine and of alcohol suggests that the effects of pyridine are due to other causes besides a lowering of the dielectric constant of the solution. Thus the experimental evidence, although not conclusive, lends weight to the hypothesis of complex formation between the pyridine and the dye. It should be stressed, however, that if complex formation occurs, then the complex is of low stability. This is shown by the following facts: (1) the spectra of the dye in aqueous pyridine (0 to 75 per cent.) have no isosbestic point*, and (2) although the molar concentration of pyridine is greatly in excess of the dye concentration, the spectrum of the dye is progressively displaced further towards the red as the pyridine concentration is increased from 10 to 75 per cent.

EXPERIMENTAL DETAILS AND RESULTS

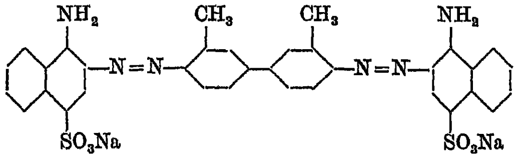
Purification and Constitution of the Dyes

A pure sample of meta-Benzopurpurine 4B was supplied by Messrs. Imperial Chemical Industries (Dyestuffs) Ltd. The other dyes were received in batch form and were purified by the method of Robinson and Mills[8]. The purified dyes were dried at 90° C. in a vacuum oven and standard solutions were prepared from the dry samples.

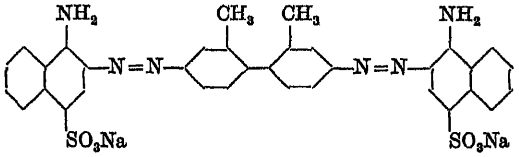
**Isosbestic Point* If two compounds, each obeying Beer's Law, are in equilibrium (*e g* the yellow and red forms of methyl orange) then when the total molar concentration of the solution is maintained constant, and also the temperature and thickness of the solution in the optical cell, the optical density—wave-length curves of all equilibrium mixtures intersect at a common point known as the isosbestic point (*cf* Weissberger "Physical Methods of Organic Chemistry", Interscience Publishers, Inc., New York, 1946, p 776). The word is derived from the Greek (prefix "iso" and root "sbestos" meaning equal quenching), and its use in the German form "isosbestisch" was proposed by Thiel, Dassler and Wulfken (1924). The word "isosbestic" was first introduced into English by Prideaux (*Chemistry and Industry,* 1926 45, 664, 678). Clark ("Determination of Hydrogen Ions", Baillière, Tindall and Cox, London, 3rd edition, 1928, p 153) referring it to this source, used the spelling "isobestic" which has been adopted by some other authors.

The constitution of the dyes are as follows:

Benzopurpurine 4B. (C.I.448) Mol. Wt 724·7

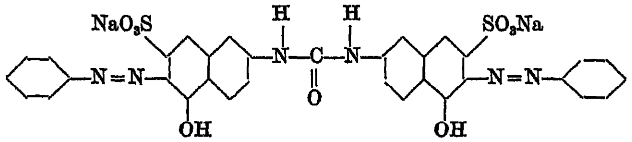


Meta-Benzopurpurine 4B Mol. Wt. 724·7

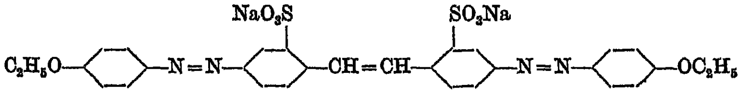


Direct Fast Orange SE. (C.I.326; Schultz 305) Mol. Wt. 756·7

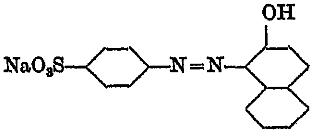
Probably.



Chrysophenine G. (C.I.365) Mol. Wt. 680



Naphthalene Orange 2G. (C.I.151) Mol. Wt. 350·3



Spectrophotometric Measurements

The absorption spectra of the dye solutions were measured in a 1 cm glass cell by means of a photo-electric spectrophotometer. The solutions were at room temperature and were not thermostatted during measurement. Most of the solutions were measured one hour, one day and one week after their preparation in order to detect any dependence of the spectrum upon the age of the solution.

In the following Tables the data are given as molar extinction coefficients ε_λ which are defined by the relation

$$\varepsilon_\lambda = \frac{1}{ct}\log_{10}\frac{(I_0)_\lambda}{(I)_\lambda}$$

where $(I_0)_\lambda$ is the intensity of light of wave-length λ transmitted by a thickness t cm. of solvent, and $(I)_\lambda$ is the intensity of light of wave-length λ transmitted by the same thickness of solution of molar concentration c

The absorption spectra of the pure dyes in water are given in Table I.

Table I
Absorption Spectra of the Dyes in Water

Dye 1	Benzopurpurine 4B	10 mg./l.	$1{\cdot}38 \times 10^{-5}$M.
Dye 2.	Meta-Benzopurpurine 4B.	10 mg./l	$1{\cdot}38 \times 10^{-5}$M.
Dye 3	Direct Fast Orange SE	7·5 mg./l.	$0{\cdot}991 \times 10^{-5}$M.
Dye 4	Chrysophenine G.	10 mg./l.	$1{\cdot}47 \times 10^{-5}$M
Dye 5	Naphthalene Orange 2G	10 mg./l	$2{\cdot}855 \times 10^{-5}$M.

Molar Extinction Coefficients $\times 10^{-4}$

Wavelength mμ	Dye 1	Dye 2	Dye 3	Dye 4	Dye 5
380	—	—	—	4·26	—
385	—	—	—	4·46	—
390	—	—	—	4·50	0·79
395	—	—	—	4·53	—
400	1·74	1·72	2·51	4·48	0·90
405	—	—	—	4·30	—
410	—	—	—	4·13	0·99
415	—	—	—	3·94	—
420	2·11	2·37	2·88	3·75	1·05
425	—	—	—	3·58	—
430	—	2·60	—	3·39	1·12
435	—	—	—	3·26	—
440	2·88	2·89	3·42	3·10	1·27
445	—	—	—	2·96	—
450	—	3·18	—	2·79	1·51
455	—	3·31	—	2·61	—
460	3·71	3·43	4·40	2·38	1·81
465	—	3·54	—	2·19	—
470	4·17	3·64	5·06	1·95	2·13
475	—	3·70	—	1·69	2·27
480	4·62	3·72	5·88	1·44	2·35
485	4·82	—	6·25	1·20	2·36
490	4·99	3·54	6·51	0·97	2·33
495	5·10	—	6·57	—	2·28
500	5·12	3·14	6·52	—	2·20
505	5·01	—	6·40	—	—
510	4·85	2·53	6·32	—	1·97
515	4·65	—	6·29	—	—
520	4·38	1·85	6·22	—	1·47
525	—	—	5·95	—	—
530	3·84	1·25	5·47	—	0·80
540	3·26	—	3·73	—	—
550	2·55	—	1·78	—	—
560	1·81	—	—	—	—

Spectral Effect of Sodium Chloride

The dye solutions containing sodium chloride were prepared at room temperature in the following way to ensure that the concentration of salt in solution during the addition of the dye did not greatly exceed that of the measured solution Ten c.c. of 0·1 g./l. dye solution were pipetted into about 85 c.c. of sodium chloride solution and distilled water was then added until the final volume was 100 c.c.

(1) *Benzopurpurine 4B.* As shown in Table II the maximum extinction coefficient ε_{max} of the dye in water depended not only on the concentration of added salt but also on the age of the solution. The latter effect is particularly marked for solutions containing 3 g. and 4 g. sodium chloride per litre.

(2) *Meta-Benzopurpurine 4B* Whereas Benzopurpurine 4B is precipitated from an aqueous 10 mg./l solution by the addition of about 6 g. sodium chloride per litre, meta-Benzopurpurine 4B remains in solution even when the salt concentration is 100 g./l. It was observed, however,

that although 10 mg./l. meta-Benzopurpurine 4B solutions containing 100 g. sodium chloride per litre were stable for a week after their preparation, solutions containing 10 g. or 50 g. salt per litre were not stable. The dye precipitated from these solutions within a few days of their preparation.

Table II

Maximum Extinction Coefficients of Benzopurpurine 4B in Aqueous Solution containing Sodium Chloride

Dye concentration · 10 mg./l. $\equiv 1{\cdot}38 \times 10^{-5}$M. ε_{max} (no salt) $= 5{\cdot}12 \times 10^4$.

NaCl. g./l.		Age of solution		
		1 hour	1 day	1 week
1	$\varepsilon_{max} \times 10^{-4}$	4·94	4·93	4·90
2		4·88	4·77	4·75
3		4·62	4·11	4·07
4		3·74	3·98	4·00

As shown in Table III the maximum extinction coefficient ε_{max} of the dye in aqueous solution containing sodium chloride depends upon the salt concentration and slightly upon the age of the solution. Except for the solution containing 50 g. salt per litre the maximum extinction coefficient of each solution changes only by about 1 per cent. during the first 24 hours after preparation.

Table III

Maximum Extinction Coefficients of meta-Benzopurpurine 4B in Aqueous Solution containing Sodium Chloride

Dye concentration 10 mg./l $\equiv 1{\cdot}38 \times 10^{-5}$M ε_{max} (no salt) $= 3{\cdot}72 \times 10^4$

NaCl g./l		Age of solution		
		1 hour	1 day	1 week
1	$\varepsilon_{max} \times 10^{-4}$	3·62	3·59	3·59
2		3·53	3·50	3·47
10		3·08	3·05	Dye pptd
50		2·62	2·48	
100		2·75	2·78	2·83

(3) *Direct Fast Orange SE.* The absorption spectra of aqueous 10 mg./l. Direct Fast Orange SE solutions containing sodium chloride (1 to 4 g./l.) do not alter significantly during the week following their preparation. Table IV shows the variation of the maximum extinction coefficient with the sodium chloride concentration.*

Table IV

***Maximum Extinction Coefficients of Direct Fast Orange SE in* Aqueous Solution containing Sodium Chloride**

Dye concentration 7·5 mg./l $\equiv 0{\cdot}991 \times 10^{-5}$M

NaCl (g./l.)	0	1	2	3	4
$\varepsilon_{max} \times 10^{-4}$	6·57	6·44	6·29	6·21	6·13

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* Fig. 4 of an earlier paper[1] showed the absorption spectra of aqueous Direct Fast Orange SE solutions containing sodium carbonate. In this figure the spectra C and A were incorrectly lettered, the letters A and C in the figure should be interchanged, i.e., the maximum coefficient of the dye decreases as the sodium carbonate concentration is increased.

(4) *Chrysophenine G.* In aqueous solution this dye is phototropic and the solutions were therefore illuminated for 15 mins. before measurement and were illuminated again when about half of the spectrum had been measured. The maximum extinction coefficient of the dye was practically independent of the concentration (0 to 4 g./l.) of sodium chloride present in the solution.

Spectral Effect of Ethyl Alcohol

The absorption spectra of Benzopurpurine 4B (10 mg./l.) in aqueous ethyl alcohol free from sodium chloride depends upon the age of the solution. As shown in Table V the decrease in the maximum optical density of a solution during a week depends on the percentage of alcohol in the solution; the decrease is greater however when the alcohol concentration is 25 per cent. than when it is 50 per cent.

Table V
Variation of the Maximum Optical Density of Benzopurpurine 4B (10 mg./l.) in Aqueous Alcohol with the Alcohol Concentration

	Cell 1 cm.			
% EtOH :—	0	25	50	98
Age of solution	Maximum optical density			
1 hour . . .	0·706	0·742	0·771	0·784
1 day . . .	0·705	0·700	0·754	0·781
1 week... ..	0·705	0·519	0·707	0·785

Similar changes with time occur with salt-free solutions of meta Benzopurpurine 4B in aqueous alcohol. Thus the maximum optical density of a meta-Benzopurpurine 4B solution containing 10 per cent. ethyl alcohol decreases by about 21 per cent. in seven days, whereas the corresponding decrease of a solution containing 90 per cent. alcohol is only about 2 per cent.

Some of the experimental work was done by Mr. A. W. Titley and Miss M. Bilsbury.

REFERENCES

[1] Holmes and Standing *Shirley Inst. Mem.*, 1944-45, 19, 260 or *Trans Faraday Soc.*, 1945, 41, 542.
[2] Valko. *Trans. Faraday Soc.*, 1935, 31, 278
[3] Robinson *Proc Roy Soc. A* , 1935, 148, 681.
[4] Neale and Stringfellow. *J. Soc. Dyers and Colourists*, 1943, 59, 241
[5] Sheppard and Geddes *J Amer Chem. Soc.*, 1944, 66, 1995.
[6] Lenher and Smith *J Phys Chem* , 1936, 40, 1005.
[7] Wyman. *J. Amer Chem. Soc* , 1931, 53, 3292.
[8] Robinson and Mills. *Proc Roy. Soc. A* , 1931, 131, 576.

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41—THE EFFECTS OF A POLYETHYLENE OXIDE CONDENSATE AND SOME POLYETHYLENE GLYCOLS ON THE ABSORPTION SPECTRA OF CERTAIN AZO DYES

By J. T. MARTIN and H. A. STANDING

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ABSTRACT

The presence of Dispersol A, a polyethylene oxide condensate, in an aqueous 10 mg /l Benzopurpurine 4B solution has a considerable effect upon the absorption spectrum of the dye. The spectral effect is similar to that of pyridine, and is independent of the Dispersol A concentration over the range 0·5 to 10 per cent The absorption spectra of the dye (10 mg./l.) in solutions containing less than 0·5 per cent. Dispersol A depend on the Dispersol A concentration, and have an isosbestic point

One per cent. Dispersol A has also a considerable effect on the absorption spectra of other azo dyes, the spectral effect with each dye being similar to that of pyridine. It is suggested that these dyes can combine with the polyethylene oxide condensate to form complexes.

The presence of 1 per cent. of a polyethylene glycol in an aqueous Benzopurpurine 4B solution has an effect similar to that of Dispersol A on the absorption spectrum of the dye The effect, however, is greater the greater the mean molecular weight of the polyethylene glycol. With any one polyethylene glycol, the presence of 5 per cent. polyethylene glycol in the aqueous dye solution has a greater effect than has 1 per cent. on the spectrum of the dye Similar results are obtained with the other azo dyes, meta-Benzopurpurine 4B and Direct Fast Orange SE

With each of these dyes the spectral effect of 1 per cent. of the polyethylene glycol of highest molecular weight is less than the spectral effect of 1 per cent. Dispersol A. Moreover the spectral effect of Dispersol A, unlike that of the glycol, reaches its maximum at a very low concentration. It is therefore suggested that although the polyethylene glycol may form a complex with the dye, the dye-glycol complex is less stable than the dye-condensate complex It is further suggested that the difference in stability of the complexes is due to the presence of micelles in the condensate, but not in the glycol, solution

INTRODUCTION

Taylor and Simon[1] have advocated the use of polyethylene oxide condensates as an aid to the spectrophotometric analysis of dye solutions They observed that the absorption spectrum of Diamine Fast Red F (Colour Index 419) in aqueous solution containing 1 per cent. of a polyethylene oxide condensate was unaffected by the addition of 1 per cent. of sodium chloride to the solution although the salt produced a large fall in the maximum extinction coefficient when the condensate was absent. They also observed that the absorption spectra of many dyes were significantly altered by the presence of the condensate in the dye solutions; and that the absorption spectra of the two dyes Chrysophenine G (Colour Index 365) and Diamine Sky Blue FF (Colour Index 518), in solutions containing both, were additive when 1 per cent. of the condensate was present, though they are not additive in pure aqueous solutions.

The similarity between these effects of a polyethylene oxide condensate on the spectra of azo dyes and the effects of pyridine—reported in the previous paper[2]—led to the work described in the present paper. This is an investigation of the effect of a polyethylene oxide condensate on the spectra of the dyes used in the previous work, namely, Benzopurpurine 4B (Colour Index 448), its meta isomer (meta-Benzopurpurine 4B), Direct Fast Orange SE (Colour Index 326), Chrysophenine G (Colour Index 365) and Naphthalene Orange 2G (Colour Index 151). The effect of a related class of compounds—the polyethylene glycols—on the absorption spectra of these dyes in aqueous solution was also investigated.

The polyethylene oxide condensate was manufactured by Messrs. I.C.I. (Dyestuffs) Ltd., and was used in the form in which it is marketed, namely, an aqueous solution designated Dispersol A. The condensate is non-ionic, and has the constitution $ROC_2H_4(OC_2H_4)_nOH$, where the end-group R is a large aliphatic hydrocarbon radical. The condensate is heterogeneous in respect to the length of the polyethylene oxide chain $-(OC_2H_4)_n-$, and the average value of *n* is uncertain. In what follows, the concentration of the polyethylene oxide condensate in a solution is expressed by the percentage content of Dispersol A, and it should be remembered that the concentration of the anhydrous condensate is only about one third of this value.

The polyethylene oxide condensates are mono-alkyl ethers of the polyethylene glycols $HOC_2H_4(OC_2H_4)_nOH$, from which they differ only in possessing a fatty hydrocarbon end-group in place of a terminal hydrogen atom. The polyethylene glycols are manufactured by the Carbon and Carbide Chemicals Corporation, and are supplied as a series of anhydrous products in which the mean length of the polyethylene oxide chain increases progressively. As supplied, the different glycols are designated by numbers ranging from 200 to 6,000; these numbers are stated to be the mean molecular weights of the polyethylene glycols. The range of molecular weights corresponds to values of *n* in the general formula ranging from 3 to 135 The products of mean molecular weight below 1,000 are viscous liquids at room temperature, those of mean molecular weights 1,000 and above are water-soluble, wax-like, solids marketed under the trade name "Carbowax". They will all be referred to in the paper as polyethylene glycols, and the mean molecular weight of a particular sample will be given, when necessary, as a numerical suffix to the name. Concentrations of the glycols in solution will be given as percentage contents of the anyhydrous substances.

(I) THE SPECTRAL EFFECT OF DISPERSOL A

The absorption spectrum of Benzopurpurine 4B in aqueous solution depends on the concentration of sodium chloride[2] in the solution, the spectra of meta-Benzopurpurine 4B and Direct Fast Orange SE are similarly affected by salt. This effect is due to the aggregation of the dye by the salt The first part of the present section describes the effect of sodium chloride on the absorption spectra of these three dyes in aqueous solution containing 1 per cent. Dispersol A, the second part describes the effect of Dispersol A upon the spectra of the dyes in salt-free solution.

The absorption spectrum of Benzopurpurine 4B (10 mg./l.) in aqueous solution containing 1 per cent Dispersol A is practically independent of the concentration (0 to 50 g./l.) of sodium chloride in the solution The spectrum is also independent of the age of the solution during the week following its preparation. The following table gives the measured values of the maximum molar extinction coefficient (ε_{max}) over this wide range of salt concentrations.

NaCl (g./l.)	0	4	10	50
$\varepsilon_{max} \times 10^{-4}$	5·35	5 34	5·32	5 36

Similarly, the presence of 1 per cent. Dispersol A in an aqueous meta-Benzopurpurine 4B solution eliminates the spectral effect of sodium chloride

(0 to 100 g./l.); and the spectrum of Direct Fast Orange SE in solution containing 1 per cent. Dispersol A alters only slightly as the sodium chloride concentration is increased from 0 to 50 g./l. These results therefore lead to the conclusion that the presence of 1 per cent. Dispersol A in the aqueous dye solution prevents the aggregation of the dye by the salt.

The presence of 1 per cent. Dispersol A in an aqueous salt-free solution of Benzopurpurine 4B (10 mg./l.) has a significant effect upon the absorption spectrum of the dye. As shown in Fig. 1 the entire spectrum is displaced towards the red by the Dispersol A and the maximum extinction coefficient is increased. This spectral effect due to a low concentration of Dispersol A is similar to that of pyridine in higher concentrations; thus, as shown in Fig. 1, the spectrum of the dye in solution containing 1 per cent. Dispersol A is almost identical with that of the dye in 25 per cent. aqueous pyridine.

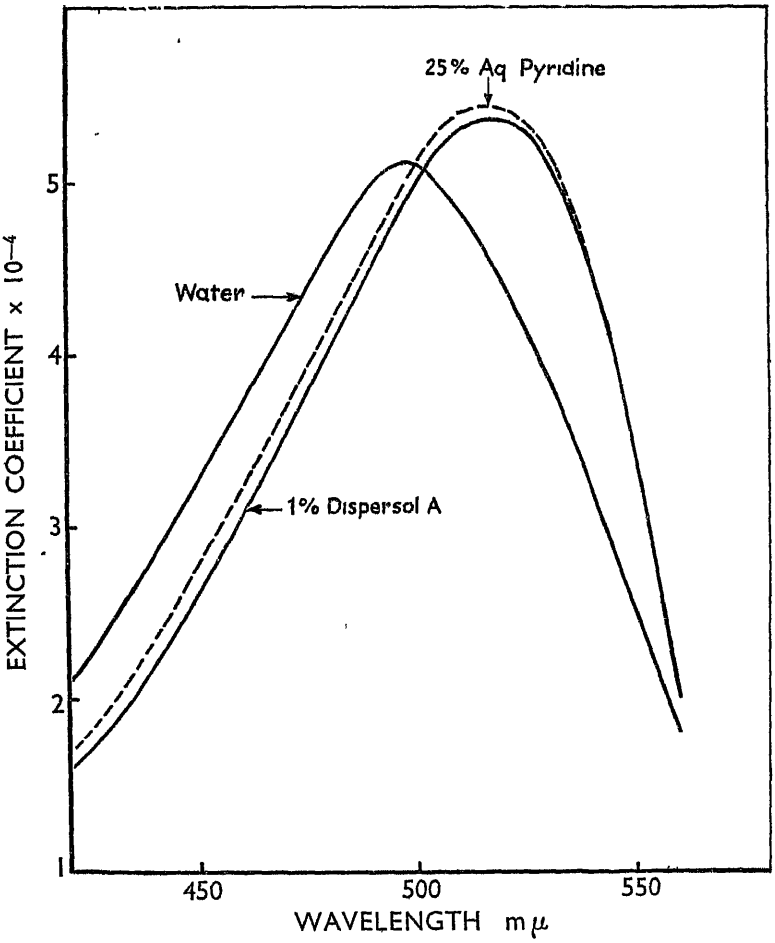

Fig. 1. Comparison of the Effects of Dispersol A and Pyridine on the Absorption Spectrum of Benzopurpurine 4B

The presence of 1 per cent. Dispersol A in an aqueous salt-free solution has also a significant effect upon the spectra of the other four dyes, as shown in Fig. 2. Thus the maximum extinction coefficient of meta-Benzopurpurine

Fig. 2. Absorption Spectra of the Dyes in Water and in 1% Aqueous Dispersol A.

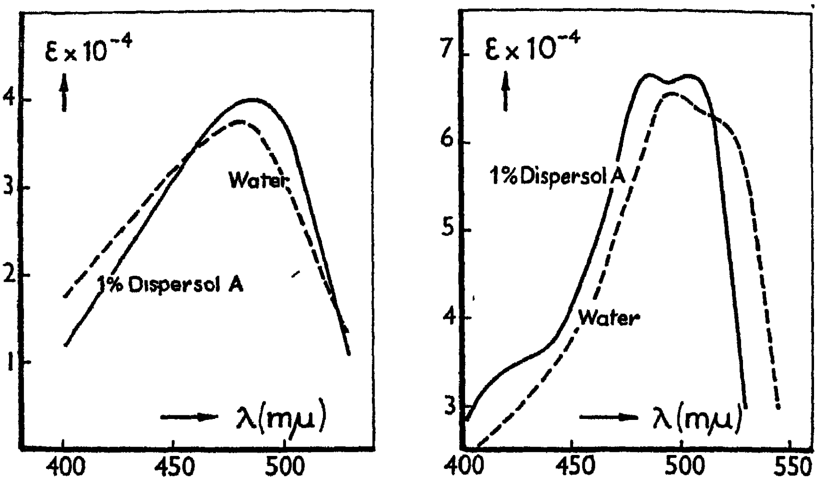

Fig 2a. Meta-Benzopurpurine 4B. (10 mg./l.)

Fig. 2b. Direct Fast Orange SE. (7·5 mg /l.)

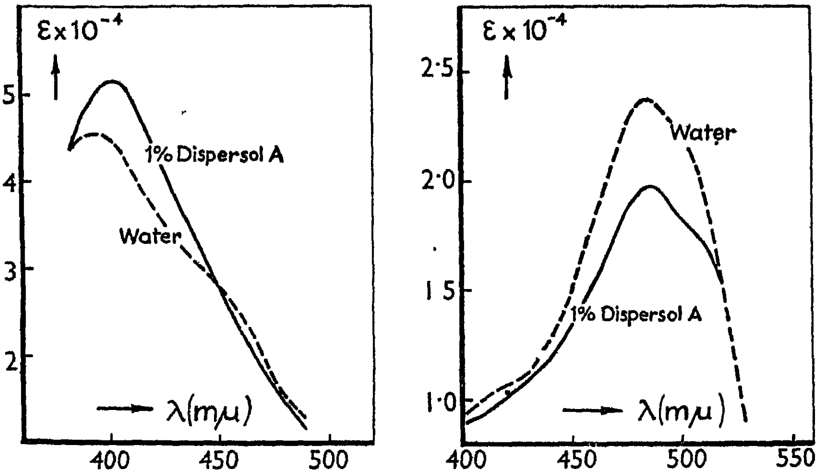

Fig. 2c. Chrysophenine G. (10 mg /l)

Fig. 2d Naphthalene Orange 2G. (10 mg /l.)

4B (Fig. 2a) is increased and the peak is displaced towards the red; the spectrum of Chrysophenine G (Fig. 2c) is similarly altered; the spectrum of Direct Fast Orange SE (Fig. 2b) is displaced towards the violet and the subsidiary peak at about 510 mμ enhanced; and the maximum extinction coefficient of Naphthalene Orange 2G (Fig. 2d) is decreased. Each of these spectral changes, due to the presence of 1 per cent. Dispersol A in the aqueous dye solution, is similar to, and comparable in magnitude with, that due to the presence of 25 per cent. pyridine in the aqueous dye solution.

The results so far described are for dye solutions containing a fixed concentration, namely, 1 per cent., of Dispersol A. When the dye concentration is maintained constant at 10 mg./l. the absorption spectrum of Benzopurpurine 4B in solutions containing Dispersol A is practically independent of the Dispersol A concentration over the range 0·5 to 10 per cent. This is shown by the following values of the maximum molar extinction coefficient ϵ_{max}, and the corresponding wavelength λ_{max}.

% Dispersol A ..	0	0·5	1	2	5	10
$\epsilon_{max} \times 10^{-4}$	5·12	5·33	5·35	5 37	5·37	5·38
λ_{max}(mμ)	498	517	517	517	517	517

Meta-Benzopurpurine 4B (10 mg./l.) behaves similarly. On the other hand, the spectra of Direct Fast Orange SE (7·5 mg./l.) and of Naphthalene Orange 2G (10 mg./l.) alter slightly as the Dispersol A concentration is increased from 0·5 to 5 per cent.

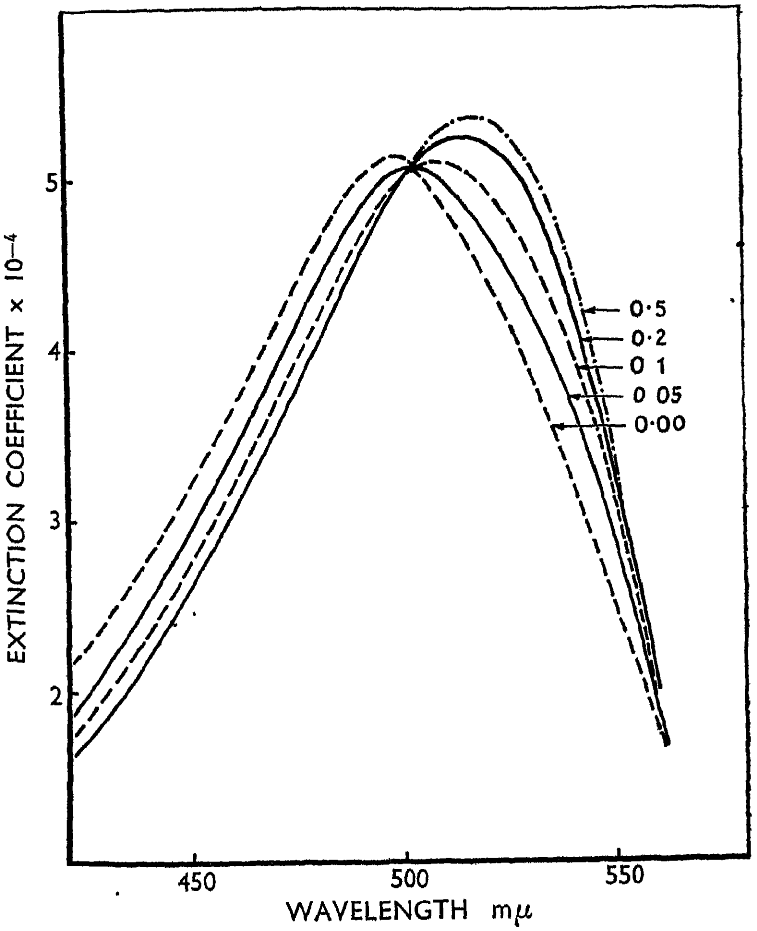

Fig 3. Absorption Spectra of Benzopurpurine 4B in Aqueous Dispersol A Solutions. Percentage by volume of Dispersol A in solution shown on each curve. Dye 10 mg./l.

Thus with Benzopurpurine 4B and meta-Benzopurpurine 4B the spectral effect of Dispersol A is considerable, and moreover is practically complete when the Dispersol A concentration attains 0·5 per cent. The effect of low concentrations (0 to 0·5 per cent.) of Dispersol A upon the absorption spectrum of Benzopurpurine 4B (10 mg./l.) is shown in Fig. 3. As the Dispersol A concentration is increased from 0 to 0·5 per cent., the maximum extinction coefficient of the dye increases and the peak is steadily displaced towards the red. Moreover these spectra have an isosbestic point at about 505 mμ. The corresponding spectra for meta-Benzopurpurine 4B also have an isosbestic point*, though not very clearly defined, at about 470 mμ.

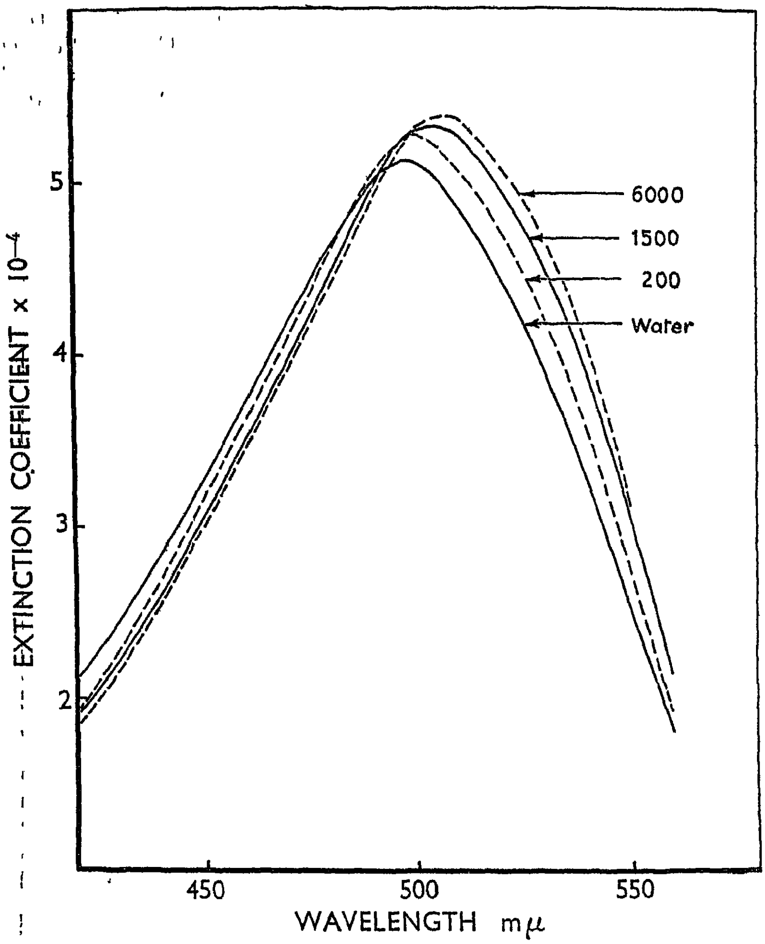

Fig. 4. Absorption Spectra of Benzopurpurine 4B in Aqueous Polyethylene Glycol Solutions
Mol. Wt of Glycol shown on each curve
Dye 10 mg/l Glycol 5%

The considerable spectral effect of 1 per cent Dispersol A strongly suggests that the polyethylene oxide condensate forms a stable complex with the dye. It was thought that complex formation might be due to weak bonding between the dye and the oxygen atoms of the polyethylene oxide chain. For this reason the spectral effect of the polyethylene glycols which contain a polyethylene oxide chain similar to that in the condensate was investigated.

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* The effect of low concentrations (0 to 0·5 per cent) of Dispersol A on the absorption spectrum of Direct Fast Orange SE (7·5 mg/l) is complex The spectra have no isosbestic point and the spectral changes are not complete when the Dispersol A concentration attains 0·5 per cent As the Dispersol A concentration is increased from 0 to 0·5 per cent the subsidiary peak at about 510mμ is at first enhanced and then decreases slightly while the broad peak at about 420 mμ is steadily developed

Fig. 5. Absorption Spectra of Meta-Benzopurpurine 4B and Direct Fast Orange SE in Aqueous Polyethylene Glycol Solutions.

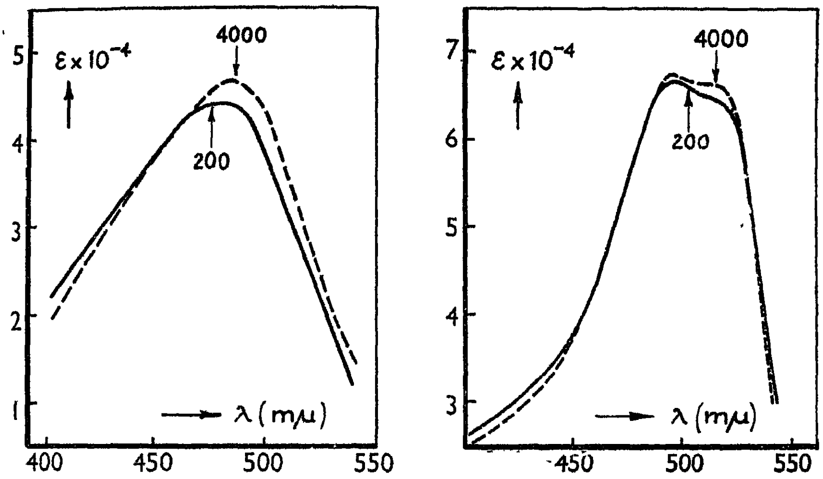

Fig 5a. Meta-Benzopurpurine 4B.
Dye 10 mg /l
Polyethylene glycol 5%
Mol Wt of glycol shown on each curve.

Fig. 5b. Direct Fast Orange SE
Dye 7·5 mg /l
Polyethylene glycol 5%
Mol. Wt of glycol shown on each curve.

(II) THE SPECTRAL EFFECT OF THE POLYETHYLENE GLYCOLS

The maximum extinction coefficient of Benzopurpurine 4B in aqueous solution containing 1 per cent by weight of a polyethylene glycol steadily decreases with time during the week following the preparation of the solution. This effect is greater with glycols of low molecular weight than with those of high molecular weight, and may be due to decomposition of the dye Meta-Benzopurpurine 4B behaves similarly, but Direct Fast Orange SE appears to be stable in the presence of the polyethylene glycols.* The absorption spectra described in this section were therefore measured immediately after the preparation of the solutions

The effect of a polyethylene glycol upon the absorption spectrum of Benzopurpurine 4B is similar to that of Dispersol A, but the magnitude of the effect depends upon the molecular weight of the glycol. This is seen from Fig. 4 which shows the absorption spectra of Benzopurpurine 4B (10 mg. /l.) in solutions containing 5 per cent by weight of the polyethylene glycols 200, 1500 and 6000 respectively. The spectral peak of the dye is raised and displaced towards the red by each glycol, the displacement, however, is greater the greater the molecular weight of the glycol. This effect is shown in greater detail by the following values of λ_{max} for 10 mg. /l. Benzopurpurine 4B solutions containing 5 per cent of a polyethylene glycol.

Mol Wt of Glycol	None	200	300	400	1500	4000	6000
$\lambda_{max}(m\mu)$	498	499	501	502	505	507	507

The effects of the polyethylene glycols on the absorption spectra of meta-Benzopurpurine 4B and of Direct Fast Orange SE also depend upon the molecular weight of the glycol. Thus Fig. 5a shows that the spectral peak of meta-Benzopurpurine 4B (10 mg. /l) is raised more, and displaced further towards the red, by 5 per cent. polyethylene glycol 4000 than by 5 per cent. polyethylene glycol 200. Similarly as shown in Fig. 5b the spectral peak of Direct Fast Orange SE (7·5 mg./l.) is raised more by 5 per cent. polyethylene glycol 4000 than by 5 per cent polyethylene glycol 200.

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* A similar difficulty, confined to the two Benzopurpurines, was encountered[2] when absorption spectra were measured for aqueous dye solutions containing ethyl alcohol.

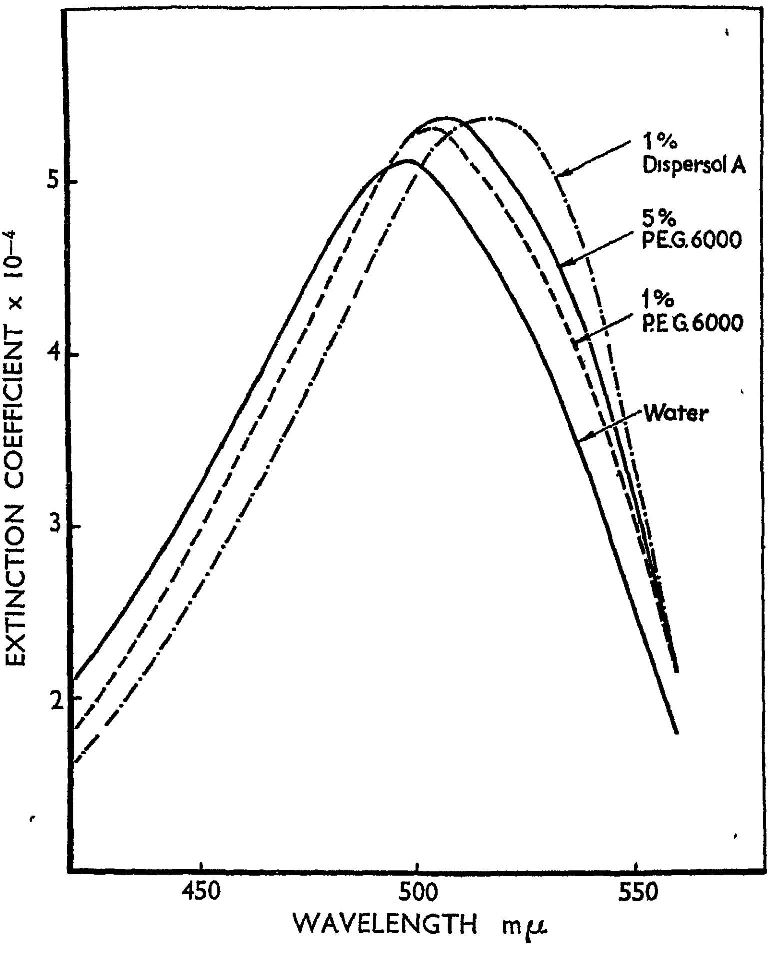

Fig 6. Absorption Spectra of Benzopurpurine 4B in Water, Aqueous Polyethylene Glycol and Aqueous Dispersol A
(Dye 10 mg /l)

The spectral effect of the polyethylene glycols depends not only on the molecular weight of the glycol but also upon the concentration of the glycol in the aqueous dye solution. Thus Fig. 6 shows that 5 per cent. polyethylene glycol 6000 in an aqueous 10 mg./l. Benzopurpurine 4B solution has a greater effect than has 1 per cent. of glycol upon the spectrum of the dye. This contrasts with the spectral effect of Dispersol A, which is the same whether the Dispersol A concentration is 1 per cent. or 10 per cent The effects of the polyethylene glycols upon the absorption spectra of meta-Benzopurpurine 4B and Direct Fast Orange SE also depend on the glycol concentration, the effect being greater with 5 per cent. than with 1 per cent. glycol.

Fig. 7. Comparison of the Effects of 1% Dispersol A and 1% Polyethylene Glycol 6000 upon the Absorption Spectra of Meta-Benzopurpurine 4B and Direct Fast Orange SE.

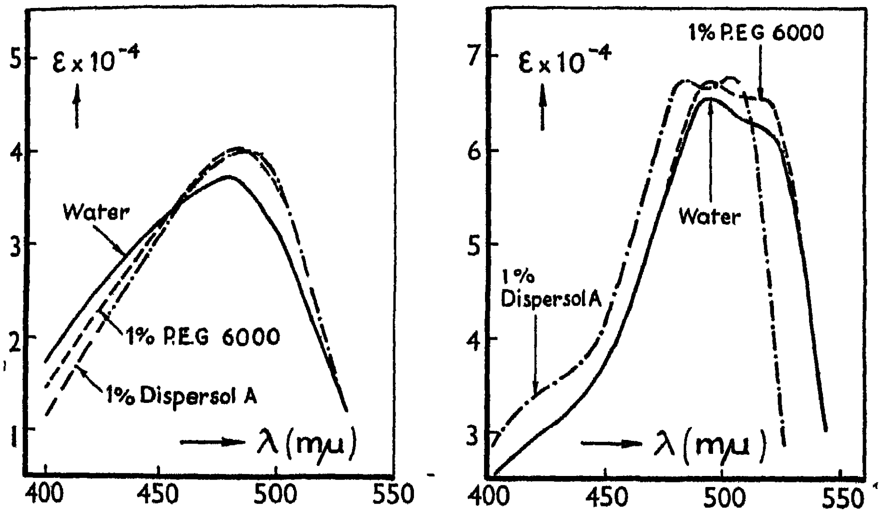

Fig. 7a. Meta-Benzopurpurine 4B. (10 mg./l.)

Fig. 7b. Direct Fast Orange SE. (7.5 mg./l.)

It is of interest to compare the magnitude of the spectral effect of the polyethylene glycols with that of Dispersol A. Since the spectral effect of the glycol increases with the molecular weight, the effect of polyethylene glycol 6000—the glycol of highest molecular weight—is compared in Fig. 6 with that of Dispersol A. This comparison is rather arbitrary in respect to concentration since Dispersol A is an aqueous solution of the condensate whereas the glycol is anhydrous; the quantitative difference between the effects of the condensate and the glycol is therefore greater even than it appears when the comparison is based, as in Fig. 6, on equal concentrations (1 per cent.) of Dispersol A and glycol. The figure shows that the absorption spectrum of Benzopurpurine 4B is displaced considerably more towards the red by 1 per cent. Dispersol A than by 1 per cent. or even by 5 per cent., of the polyethylene glycol 6000

With meta-Benzopurpurine 4B (Fig. 7a) the contrast between the spectral effects of 1 per cent. Dispersol A and 1 per cent. polyethylene glycol 6000 is much less marked; both substances displace the spectral peak of the dye by about the same amount. Over the shorter wave-lengths, however, the spectrum of the dye is displaced more towards the red by the Dispersol A than by the glycol. With Direct Fast Orange SE (Fig. 7b) the contrast between the spectral effects of the Dispersol A and the polyethylene glycol 6000 is most marked. Both substances increase the maximum extinction coefficient of the dye and develop the secondary peak at about 515 $m\mu$, but whereas the polyethylene glycol has practically no effect on the wave-length of maximum absorption, Dispersol A displaces the entire spectrum towards the violet. Thus with each of these three dyes 1 per cent. Dispersol A has a greater effect than has 1 per cent. polyethylene glycol 6000.

It has been shown that the presence of 1 per cent. Dispersol A in an aqueous 10 mg./l. Benzopurpurine 4B solution not only has a considerable effect upon the absorption spectrum of the dye, but also eliminates the effect of sodium chloride (0 to 50 g./l.) on the spectrum of the dye. The presence of 1 per cent polyethylene glycol 1540, however, in an aqueous 10 mg /l Benzopurpurine 4B solution reduces but does not eliminate the spectral effect of 4 g. sodium chloride per litre. As shown by the following table, the maximum extinction coefficient ε_{max} of the dye decreases as the concentration of sodium chloride in the solution is increased.

NaCl (g /l)	0	2	4
$\varepsilon_{max} \times 10^{-4}$	5·37	5 04	4 90

Similarly the effects of 4 g. sodium chloride per litre upon the absorption spectra of meta-Benzopurpurine 4B (10 mg./l) and of Direct Fast Orange SE (7 5 mg /l.) are reduced, but not eliminated, by the presence of 1 per cent. polyethylene glycol 1540 in the aqueous dye solutions. Thus 1 per cent. of a polyethylene glycol in the aqueous dye solution not only has a smaller effect than has 1 per cent. Dispersol A, on the absorption spectrum of the dye, but unlike 1 per cent. Dispersol A, it does not eliminate the spectral effect of sodium chloride.

DISCUSSION

It has been shown that the presence of only 1 per cent. Dispersol A in the aqueous dye solution has a considerable effect upon the absorption spectrum of the dye, the effect being similar, and approximately equal, to that of 25 per cent. pyridine Moreover when the dye solution contains 1 per cent. Dispersol A, sodium chloride has no appreciable effect upon the spectrum of an aggregating dye, a fact which shows that in the presence of Dispersol A the dye is not aggregated by salt. These results lead to the same conclusion as that previously reached by Valko[1] from aqueous diffusion measurements with Chicago Blue 6B and the non-ionic polyethylene condensate Peregal O, namely, that polyethylene oxide condensates combine with certain azo dyes to form complexes. In order to explain the present results it is necessary to make the additional assumption that the complex between the dye and the condensate is not aggregated by sodium chloride

It has also been shown (Fig. 3) that when the dye concentration is maintained constant at 10 mg /l the absorption spectra of Benzopurpurine 4B in solutions containing from 0 to 0 5 per cent Dispersol A have an isosbestic point The existence of an isosbestic point shows that, in the presence of Dispersol A, the dye exists in solution as an equilibrium mixture of two forms. This conclusion not only supports the hypothesis of complex formation between the dye and the Dispersol A, but it also shows that an equilibrium exists between the dye, the Dispersol A, and the dye-Dispersol A complex (cf. Valko[4]). As the Dispersol A concentration is increased, more dye combines with the Dispersol A and the absorption spectrum approaches that of the complex alone.* Since the absorption spectrum of the dye solution becomes independent of the Dispersol A concentration when the latter exceeds 0·5 per cent , it follows that under these conditions practically all the dye has combined with the polyethylene oxide condensate.

Benzopurpurine 4B is a weak base and behaves as an acid-base indicator. A dilute solution of the dye changes in colour from orange-red to violet-blue as the *pH* is lowered from 5 to 1·5. The blue solution of Benzopurpurine 4B (10 mg./l.) in 0·01N hydrochloric acid, but not that in 0·1N acid, changes to red on the addition of Dispersol A equivalent to 1 per cent. by volume. It has been confirmed by measurements with the glass electrode that the change in colour on the addition of the Dispersol A to the 0·01N acid solution is not accompanied by any change in *pH*. This behaviour provides further evidence of interaction between the dye and the polyethylene oxide condensate. It would be explained by the formation of a complex of lower basic strength than the free dye. No quantitative study has been made of the spectra of the dye in acid solutions because these solutions are not stable, showing a variety of ageing effects. The well-known acid-base indicator Congo Red (Colour Index 370) has the same constitution as Benzopurpurine 4B except that the benzidine nucleus in the former is replaced by the tolidine nucleus in the latter. The transition interval of Congo Red is sharper than that of Benzopurpurine 4B, namely, about *pH* 5 (red) to *pH* 3 (blue) The blue solution of Congo Red in 0·001N hydrochloric acid, but not that in 0·01N acid, changes to red without *pH* change on the addition of 1 per cent. Dispersol A. Simon and Taylor[1] observed that a large effect was produced by a polyethylene oxide condensate on the relation between the colour and the *pH* of a solution of Diamine Fast Red F.

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* An attempt was made to calculate the relative proportions of free dye and dye-Dispersol A complex from the spectra shown in Fig. 3 It was found, however, that the spectra could not be exactly resolved into a combination of the two limiting spectra corresponding to Dispersol A concentrations of 0 and 1 per cent respectively. This may be due to the fact that Dispersol A is heterogeneous in respect to the length of the polyethylene oxide chain

The effect of the polyethylene glycols upon the absorption spectra of the dyes is similar to that of Dispersol A. The magnitude of the spectral effect, however, depends upon the molecular weight of the glycol, and even with the glycol of highest molecular weight it is smaller than that of Dispersol A at comparable concentrations. Moreover the spectral effect of the condensate, unlike that of the glycol, reaches its maximum at a very low concentration. These results therefore lead to the conclusion that the glycol may form a complex with the dye but that the dye-glycol complex is less stable than the dye-condensate complex; *i e.* a much higher relative concentration of glycol than of condensate is required to convert all the dye into a complex.

This difference between the polyethylene oxide condensates and the polyethylene glycols is probably due to the fact that in the condensate, but not in the glycol, a hydrophobic end group—the hydrocarbon radical—is attached to the hydrophilic polyethylene oxide chain. Gonick and McBain[4] have shown that non-ionic polyethylene oxide condensates similar to Dispersol A exist as micelles in aqueous solution. The hydrophobic hydrocarbon radicals are probably near the centre of the micelle and the hydrophilic polyethylene oxide chains near the surface. Hence if a dye molecule becomes attached to an ether oxygen atom (or a terminal hydroxyl group) of a polyethylene oxide chain, it may become entangled and firmly held in the hydrophilic fringe of the micelle. It is possible, for example, that the dye molecule may become attached to two ether oxygen atoms, each in different polyethylene oxide chains, and favourably situated in the same micelle An alternative view is that the conditions are such as to furnish a concentration of polyethylene oxide chains much higher in the vicinity of the dye molecule than would be calculated from the overall concentration of the condensate in solution

The polyethylene glycols have no large hydrophobic groups, but contain hydrophilic groups (ether oxygen atoms) distributed along the whole length of their molecules. There is no evidence that the glycols form micelles in aqueous solution and it seems unlikely that they would Hence the chance of two polyethylene oxide chains being favourably situated for bridging by a dye molecule might be much smaller in a solution of the glycol than in a comparable solution of the condensate, alternatively, the attachment of the dye molecule in the formation of a dye-glycol complex must occur under conditions that do not provide a high local concentration of polyethylene oxide chains. Thus, on this hypothesis, the difference between the stabilities of the dye-condensate complex and the dye-glycol complex is attributed to the micellar structure of the condensate.

EXPERIMENTAL DETAILS AND RESULTS

The purification of the dyes and details of the spectrophotometric measurements have been given in the previous paper.[2]

Spectral Effect of Dispersol A

A definite percentage by volume of Dispersol A was added to the aqueous dye solutions. When the dye solution contained 1 per cent. Dispersol A, the dye was not precipitated by sodium chloride of relatively high concentration. Thus Benzopurpurine 4B is precipitated from an aqueous 10 mg./l. solution by the addition of about 6 g. sodium chloride per litre When the dye solution contains 1 per cent. by volume of Dispersol A, however, the dye is not precipitated from solution by the addition of 50 g. salt per litre. Direct Fast Orange SE behaves similarly. In this additional respect the action of Dispersol A resembles that of pyridine.

It has been stated that the absorption spectra of Direct Fast Orange SE (7·5 mg./l.) and of Naphthalene Orange 2G (10 mg./l.) in solutions containing Dispersol A alter slightly as the Dispersol A concentration is increased from 0·5 to 5 per cent. This is shown in the following table by the values of ε_{max} and λ_{max}; the values for each of the two peaks of Direct Fast Orange SE are given.

Table I

Dye		% Dispersol A (by volume)				
		0	0·5	1	2	5
Direct Fast Orange SE (7·5 mg./l.)	$\varepsilon_{max} \times 10^{-4}$	6·57	6·72	6·79	6·81	6·84
	λ_{max}(mμ)	495	493	485	484	484
	$\varepsilon_{max} \times 10^{-4}$	(6·2)	6·88	6·80	6·80	6·77
	λ_{max}(mμ)	(520)	505	505	505	504
Naphthalene Orange 2G (10 mg./l.)	$\varepsilon_{max} \times 10^{-4}$	2·36	2·08	1·98	—	1·91
	λ_{max}(mμ)	484	485	485	—	485

Spectral Effect of the Polyethylene Glycols

The maximum optical density of a 10 mg./l. Benzopurpurine 4B solution containing 1 per cent. polyethylene glycol decreases with time; the rate of the decrease being greater with glycols of low molecular weight than with those of high molecular weight. This is shown in Table II by the maximum optical densities of Benzopurpurine 4B solutions (10 mg./l.) containing 5 per cent. polyethylene glycol and measured one hour and one day after preparation.

Table II

Mol Wt. of Polyethylene glycol :—		200	300	400	4000	6000
D_{max}	1 hour	0·728	0·730	0·735	0·744	0·740
	1 day	0·693	0·680	0·721	0·745	0·741

As previously stated, the effect of a polyethylene glycol on the absorption spectrum of each dye is greater the greater the molecular weight of the glycol. The appropriate data for Benzopurpurine 4B, meta-Benzopurpurine 4B, and Direct Fast Orange SE are given in Table III. Since the spectral peaks of the Benzopurpurines are raised and displaced towards the red by the polyethylene glycols, both the values of ε_{max} and λ_{max} for these dyes are given. The spectral peak of Direct Fast Orange SE, however, is not displaced by the polyethylene glycols; their effect is rather to develop the secondary peak at about 515 mμ. Consequently only the values of the extinction coefficient at 515 mμ are given for this dye.

Table III

Benzopurpurine 4B (10 mg /l.) Polyethylene glycol 1%.

	Aqueous solution	Mol Wt of glycol				
		200	400	1500	4000	6000
λ_{max}(mμ)	498	499	500	502	504	504
$\varepsilon_{max} \times 10^{-4}$	5·12	5·16	5·24	5·27	5·30	5·30

Meta-Benzopurpurine 4B. (10 mg./l.) Polyethylene glycol. 1%.

	Aqueous solution	Mol. Wt. of glycol				
		200	400	1000	4000	6000
λ_{max}(mμ)	478	478	477	482	484	485
$\varepsilon_{max} \times 10^{-4}$.	3·72	3·78	3·79	3·86	3·99	4·02

Direct Fast Orange SE (7·5 mg /l) Polyethylene glycol 1%.

	Aqueous solution	Mol. Wt. of glycol				
		200	300	1500	4000	6000
ε at 515mμ	6·29	6·35	6·41	6·41	6·49	6·56

Some of the experimental work was done by Mr. A. W. Titley.

REFERENCES

[1] Taylor and Simon. *American Dyestuff Reporter*, 1945, 34, 319.
[2] Martin and Standing Previous paper.
[3] Valko. *J. Soc. Dyers and Colourists*, 1939, 55, 173
[4] Gonick and McBain *J Amer Chem Soc.*, 1947, 69, 334
[5] Robinson and Mills *Proc. Roy. Soc. A* , 1931, 131, 576.

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41—STATIC ELECTRIFICATION IN THE PROCESSING OF FIBRES : VARIATION WITH MOISTURE REGAIN DURING CARDING

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SUMMARY

A simple experimental technique is described by which the electrostatic charge generated by a fibre during processing can be measured. This has been applied to eight typical fibres in their passage through a cotton flat carding engine.

Figures are given for the over-all charge measured on the sliver for cotton, viscose, flax, cellulose acetate, wool, casein, Ardil and nylon at various moisture levels. The fibres divide into two groups. For wool, casein, Ardil, nylon and cellulose acetate the charge increases with decreasing regain until at levels corresponding roughly to the moisture take-up of the fibres at 60-70 per cent R.H the static electrification tends to reach a steady value of the same order for all five fibres For the cellulose fibres cotton, flax and viscose, the charges developed are much lower than for the protein fibres. The charge again increases with decreasing regain, but a constant level is not reached.

The cellulose fibres tend to be negatively charged, whilst the charge tends to be positive for the "protein" type fibres.

It is shown that the behaviour of these fibres can be explained on the assumption that the quantity of charge generated is independent of the regain of the fibre, and is of the same order for all eight fibres. As the regain of the fibre is increased, the proportion of this charge which is lost to the machine between the fibre leaving the cylinder and reaching the sliver increases, so that the nett charge carried away by the fibre decreases with increasing regain By the use of resistance-regain relations, specially determined for this investigation, the electrification curves can be calculated with one fitted constant There is reason to believe that the capacitance per unit length of fibres for wool, nylon, Ardil and acetate is independent of regain, but that the capacitance of the cellulosic fibres increases rapidly with increasing moisture regain.

INTRODUCTION

Although the electrification of fibres (now commonly referred to as "static") is one of the important factors in textile processing about which much superficial knowledge has been gathered, very little work has been done on the quantitative measurement of the charges generated

With the development of new fibres, the need for more exact information has become urgent, for in the evaluation of these fibres on textile machinery, it is usually not easy to analyse difficulties, and static electrification tends to be introduced in many cases as a convenient explanation Also, in the development of anti-static agents and devices, a quantitative method of measurement is of paramount importance.

This paper describes such a method and gives the results of a preliminary study of the electrification acquired during the carding of some of the more common fibres A mechanism of control of the charge by leakage is suggested It must be emphasised that the work is purely exploratory and that no high accuracy is claimed.

APPARATUS

The static electrification produced on fibres during processing is extremely difficult to remove owing to the high resistance of the mass of fibres. Here the small area of contact from fibre to fibre undoubtedly plays an important part. If, however, electrically charged fibres are placed inside an insulated metal container or Faraday cylinder, a charge, equal to the nett charge on the fibres, will be induced on the outside of the container If the capacitance of the system is known, measurement of the voltage generated on the container system will give a measure of the over-all charge on the fibre mass.

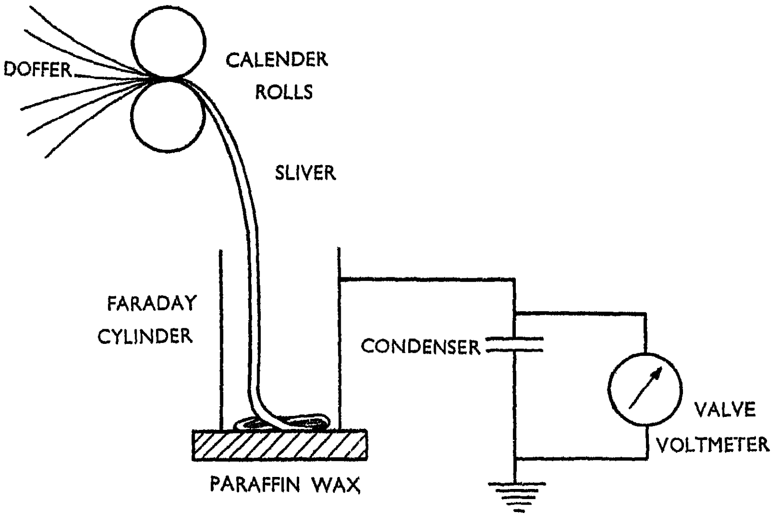

Fig 1.
Apparatus for measuring electrostatic charge on fibres during carding

This system was adopted, the arrangement being shown in Figure 1. The Faraday cylinder consisted of a two gallon galvanised bucket, insulated by standing on a block of paraffin wax approximately 2 in. thick. The cylinder was connected to a calibrated condenser, the capacitance of which could be varied from 1·0 to 0·01 μF to give suitable voltages for measurement, and the voltage was determined using a backed off transconductance valve voltmeter employing an electrometer triode

EXPERIMENTAL PROCEDURE

In practice the fibre was allowed to fall into the Faraday cylinder and the voltage was read. After a number of preliminary experiments with different types of fibre handling machinery, a revolving flat cotton carding engine was chosen as the most suitable machine for these tests The sliver from this machine, after passing through the calender rolls, fell straight into the Faraday cylinder instead of being led into the sliver can At a convenient voltage reading the sliver was broken off and the amount collected in the cylinder was weighed. Tests showed that, for given conditions, the charge carried by the sliver into the Faraday cylinder was proportional to the weight of the sliver, and the charge was accordingly expressed as microcoulombs per gram of fibre

The charge generated by any other machine could be determined in the same way, preferably by letting a sufficient amount of fibre fall freely into the cylinder. Where the charge to be measured is small, however, condensers of smaller capacitance must be used, and special precautions taken against accidental leaks. This might not always be easy in a factory in normal production.

The revolving flat cotton carding engine used was of standard type made by Messrs. Howard & Bullough, Ltd., 45 in. wide with the main cylinder 50¾ in. in diameter. The speeds were:—cylinder 160 r.p.m., taker-in 365 r.p.m., and doffer 5 r.p.m. The clearance settings were:—taker-in to cylinder 0·007 in., flats to cylinder 0·012 in., and doffer to cylinder 0·007 in. These settings were used unchanged for all the fibres tested.

The moisture regains of the fibres were controlled by varying the relative humidity of the room containing the card. This was normally controlled to be 65 per cent. at 70° F. As there was no refrigerating or dehydrating mechanism in the controlling system, however, it was necessary, in order to obtain low humidities, to raise the temperature of the room—for 18·5 per cent. R.H. the room temperature was raised to 95° F. For humidities higher than 65 per cent., the temperature was roughly constant at 70° F., as these high humidities were within the capacity of the water sprays on the control system, although for 95 per cent. R.H. some help from an open steam jet was required.

The fibres, in the form of laps, were conditioned overnight, *i.e.* for a period of 18 to 20 hours, and were then run on the card. For each run moisture determinations were made on duplicate samples taken from the sliver during the static electrification determinations, and it is on these moisture values, and not on the relative humidity levels necessary to obtain them, that discussion is based. The laps were prepared on a normal scutcher and were conditioned in the roll form. It is reasonable to suppose that at least the outer layer (say ½ in. thick) would be fairly uniformly conditioned by the overnight exposure to the chosen relative humidity, and runs were kept short so that in each case only this outer layer was used. Variations in moisture regain were, in many cases, easily observed by changes in the static readings. In three cases, for cotton and viscose with around 2 per cent. moisture, tested at 18·5 per cent. R.H., the fibre had been dried in an oven and was not in equilibrium with the atmosphere. These readings were taken in an attempt to raise the level of static electrification for these cellulose fibres to that of the protein fibres.

Eight types of fibre were used, particulars being as follows:—

Cotton:—1¼in. staple Peruvian.
Flax:—Irish, cut to 1½ in. staple.
Viscose:—Standard bright Fibro, 1$\frac{7}{16}$ in. staple, crimped, 3 denier (diameter 18 μ).
Wool.—60's Merino, cut top, 1½ in. staple.
Ardil.—1½ in. staple, made from ground nut protein at Ardeer, 5·5 denier (diameter 25 μ).
Casein:—1½ in. staple, made from casein at Ardeer, 5·5 denier (diameter 25 μ).
Acetate.—1$\frac{7}{16}$ in. staple, delustred and crimped, 2·4 denier.
Nylon.—1$\frac{7}{16}$ in. staple, delustred and crimped, 3·2 denier (diameter 21 μ).

These fibres were used as received and should be representative of commercial products.

Table I

Electrostatic charges generated on fibres during carding on a flat cotton card

Material	Moisture gm /100 gm dry fibre	log charge $\frac{\mu c}{gm}$	Sign of Charge	Workability
Cotton	1·6	$\bar{2}$·35	−	Good
	2·0	$\bar{2}$·24	−	
	3·1	$\bar{3}$·57	−	
	5·1	$\bar{4}$·77	−	
	5·2	$\bar{4}$·94	−	
	6·4	$\bar{5}$ 42	−	
Flax	6·0	$\bar{3}$·52	+	Unworkable
	8·0	$\bar{4}$·42	+	
	8 15	$\bar{4}$ 51	−	
	8·9	$\bar{4}$·20	−	
	9·1	$\bar{5}$·40	−	
	13·9	$\bar{6}$·60	−	
Viscose	2·5	$\bar{2}$·68	−	Poor
	9·9	$\bar{5}$·18	−	Good
	10·0	$\bar{5}$·94	+	
	10·2	$\bar{4}$·32	−	
	10 3	$\bar{4}$·65	+	
	15·3	$\bar{6}$·53	−	
	18·2	$\bar{7}$·08	+	
Nylon	2·6	$\bar{2}$·40	+	Good
	2 9	$\bar{2}$·53	+	
	3·2	$\bar{2}$·67	+	
	3·55	$\bar{2}$ 56	+	
	3·55	$\bar{2}$·59	+	
	4·0	$\bar{2}$ 53	+	
	4·2	$\bar{2}$·43	+	
	4·7	$\bar{2}$·08	+	
	5·0	$\bar{2}$·04	+	
	5·5	$\bar{6}$·50	−	
	5·9	$\bar{3}$ 28	+	
	6·0	$\bar{4}$·93	+	
Acetate	3·1	$\bar{2}$·34	−	Unworkable
	4 7	$\bar{2}$ 04	−	
	5·6	$\bar{2}$·12	−	
	5·8	$\bar{3}$ 97	−	Poor
	5·95	$\bar{2}$·00	−	
	6·0	$\bar{2}$·01	−	
	6·15	$\bar{2}$ 23	−	
	7·7	$\bar{3}$·95	−	Good
	9·85	$\bar{4}$·60	−	
Casein	9·4	$\bar{3}$ 92	+	Unworkable
	9·9	$\bar{3}$ 91	+	
	11 1	$\bar{3}$ 93	+	Poor
	11 2	$\bar{3}$·50	+	
	11·55	$\bar{3}$·89	−	
	12·4	$\bar{5}$·10	−	Good
	12·7	4·46	−	
	14·0	$\bar{5}$·57	−	
Ardil	10·7	$\bar{2}$ 07	+	Unworkable
	11·25	$\bar{2}$ 11	−	
	11·25	$\bar{2}$·04	−	
	11·5	$\bar{3}$·83	+	
	12·05	$\bar{3}$·36	−	Poor
	12 3	$\bar{3}$·59	+	
	12 7	4·54	+	Good
	14·1	$\bar{5}$·75	+	
Wool	9 3	$\bar{2}$·15	+	Unworkable
	10 8	$\bar{2}$·40	+	
	11·6	$\bar{2}$ 15	+	
	11 75	[illegible] 46	+	
	12·7	[illegible]·46	+	Poor
	12 9	2·04	+	
	13 0	$\bar{2}$·30	+	
	13·35	$\bar{2}$ 11	+	Good
	18·8	$\bar{4}$·43	+	
	20·6	$\bar{5}$·60	−	

Each type of fibre was run through the card in turn at each humidity level. The card was run empty for 30 minutes and the cylinder doffer and flat wires were cleaned after each kind of fibre. During each run, several measurements of charge were made for various weights of fibre, and the mean result taken, expressed as microcoulombs per gram of fibre. At the same time, two samples of sliver were collected in weighing bottles and the regain was found from the loss in weight after heating for two hours at 110° C. expressed as a percentage of the dry weight The mean of these

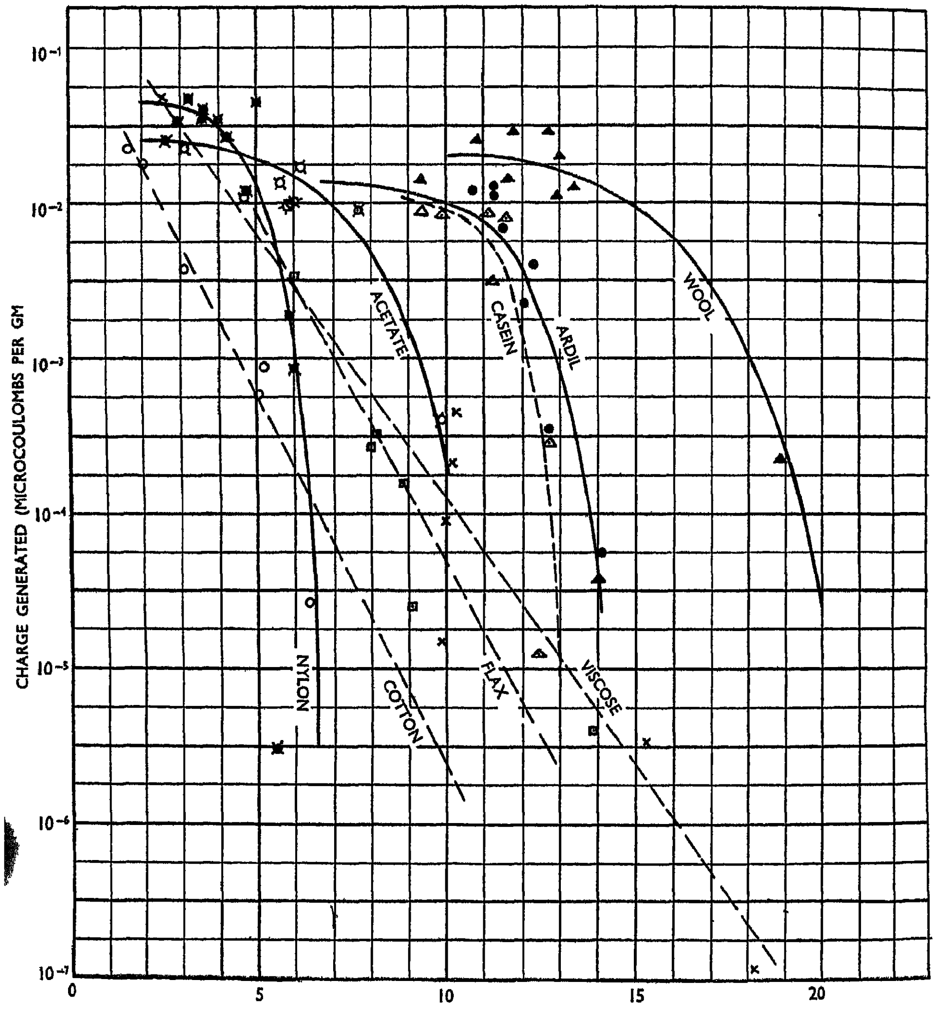

Fig 2

Electrostatic charge on fibres after carding at varying moisture regains

● Ardil ⌑ Acetate △ Casein ○ Cotton ☐ Flax ✖ Nylon. × Viscose ▲ Wool

Full lines calculated from $K=R[\log_{10}Q_0-\log_{10}Q]$ (Q and Q_0 in microcoulombs per gram, R in megohm cm)

Values used	*Wool*	*Ardil.*	*Nylon.*	*Acetate*
K	$\underline{2}\ 90$	$\underline{1}\cdot 58$	$\underline{2}\ 53$	$\underline{3}\ 20$
$\log_{10} Q_0$	$\bar{2}\cdot 30$	$\bar{2}\cdot 13$	$\bar{2}\ 65$	$\bar{2}\cdot 40$

Dotted lines are drawn through experimental points.

two values was taken as the regain.* The sign of the charge was evident from the direction of the deflection. The experimental results obtained are set out in Table I and are plotted in Figure 2.

Effect of Static Electrification on the Carding of Fibres

In each experiment the running of the machine was rated by an experienced cotton operative with regard to the behaviour and ease of handling of the web. In certain cases, where the electrification was severe, it was still possible to form a good web and condense it to sliver even though the sliver tended to cling to the machine. Column 5 in Table I gives these results, where the charge level for a good web is indicated. Cotton and nylon formed good webs, even with relatively high electrostatic charges; flax was very poor.

The case of cotton was particularly interesting. The very low regains of around 2 per cent. were obtained by heating the lap overnight at 130° C. At this low moisture regain in an atmosphere of 18·5 per cent R.H. and 95° F. the electrification was considerable, but in spite of this, the web could be readily collected and the sliver led away in spite of a tendency to stick to the rolls.

It would appear that the controlling factor in the formation of the web is crimp—the cotton, nylon and acetate fibres used were highly crimped and tended to give a strong web, whilst the straight flax fibre was almost unworkable, even at relatively low levels of electrification. The crimp of the other fibres fell between these extremes.

In the case of nylon the cylinder wires tended to fill up and choke. This was thought to be due to the very high degree of crimp on this fibre—30 to the inch.

Sign of Charge (*See Table I.*)

For relatively high regains, when the charge on the fibre was very low, the sign of the charge for any material appeared to be uncertain and to vary from positive to negative for consecutive runs, or even to change during a single run. When strong electrification occurred, however, at lower regain, the sign of the charge was quite definite except in the case of flax, Ardil and casein where an inversion occurred.

In these experiments, of course, only the nett charge on the sliver was determined, and there was no certainty that all parts of the sliver had the same sign of charge.

For strong electrification the fibres fell into two groups—the cellulose fibres, viscose, cotton, flax and cellulose acetate, which tended to be negatively charged, and the protein fibres, wool, casein, and perhaps Ardil, which, together with nylon, tended to be positively charged. It was not certain if this was a general rule, as further experiments gave indications that protein fibres might, in some circumstances, become negatively charged If, however, there was a general tendency for fibres in these two groups to develop charges of opposite sign, this would have an important bearing on the processing of mixtures of fibres from the two groups, say, viscose and nylon.

VARIATION OF ELECTROSTATIC CHARGE WITH REGAIN OF THE FIBRE

The results in Table I are shown graphically in Figure 2, in which the charge in microcoulombs per gram of sliver is plotted against the regain.

For wool, Ardil, casein, cellulose acetate and nylon, the charge increases at first with decreasing regain, but for the lower regains the curve flattens and the charge tends to assume a steady value. There is in all these curves a change of slope which occurs for each fibre at a moisture level roughly corresponding to its normal moisture of condition at around 60-70 per cent. R.H The constant value reached by the charge on these five fibres is of the same order, lying between 0·01 and 0·08 microcoulombs per gram of fibre, while the total range of charges is about ten thousand times for the whole curve.

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* Refer BS 1051: 1942;

In contrast to this, the curves for the cellulose fibres, cotton, flax and viscose, form a group which shows no such inflexion. Here the points lie roughly on straight lines, even for values of moisture regain very much below the normal moisture regain at 60-70 per cent R H. In the case of cotton and viscose the curves are still straight lines at regains of 2 per cent. compared with normal moisture regains of around 7 per cent. and 11 per cent. respectively at 60-70 per cent. R.H Only at this low regain do the charges on the cellulose fibres reach the steady values for the "protein" group.

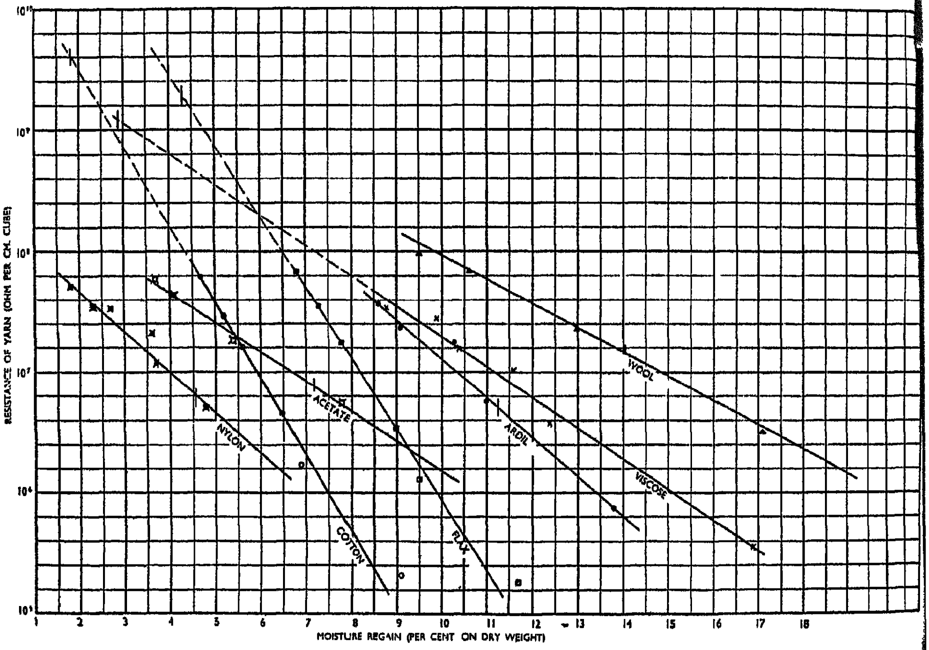

Fig. 3
Variation of resistance of yarns with moisture regain.

It was not possible, during these experiments, to do trials on cellulose fibres at regains below 2 per cent., so that the important question as to whether cellulose fibres actually did generate higher charges than the "protein" group remains unsettled, as does the problem as to whether the curves for these fibres flatten at higher static values.

A Suggested Mechanism Controlling the Charge acquired by a Sliver

The fact that the maximum charge, generated at very low regains, is of the same order for five different fibres suggests that it is not dependent on the nature of the fibre, but on the process—carding—or possibly on the machine, *i.e* the card. On this supposition, so violent is the treatment of the fibres in the card that the maximum possible charge for the process is always generated on them, independent of their regain.

The fact that, at higher regains, the fibres leaving the machine have much smaller charges, does not necessarily imply that smaller charges have been generated. Exactly the same behaviour would be observed if the charge generated were constant, but the quantity of charge which leaks away during the carrying of the fibre on to the doffer and from the doffer to the sliver can varies with the regain.

Now the rate of loss of charge will depend primarily on the electrical resistance of the fibre, and this may be expected to decrease as the regain of the fibre is increased.

It is, of course, the resistance, both axial and transverse, of single fibres which controls the leakage of charge during the passage through the carding engine. The direct measurement of such a resistance would be a very difficult experiment, but the resistance of a yarn corresponding to an assembly of very large numbers of fibres should be proportional to the individual fibre resistance. Measurements of the resistance of lengths of yarns, made from the same materials as were used in the electrification tests, have been made.

The experimental methods used are described in the Appendix, and the results are plotted in Figure 3 which shows that the resistance decreases approximately exponentially with increase of regain The tests were made at a fixed potential difference of 18 volts. No attempt was made to investigate the variation of resistance with applied voltage, as the voltage appropriate to leak conditions in the cotton card is not known The results obtained in the experiments of the Appendix were intended purely to determine a resistance proportional to that controlling the leak of charge from a fibre during carding and therefore contain an unknown constant of proportionality. It was, for this reason, decided in this preliminary study to restrict these tests to the limiting range of test conditions described in the Appendix.

Using these results to determine constants in the normal leakage equation, it is possible to calculate curves relating charge and moisture regain for comparison with the experimental results.

For an element of capacitance C and leak resistance R, if the total time for which leakage takes place is t, then the relation between final charge Q and initial charge Q_0 is

$$\log_e Q = \log_e Q_0 - t/CR \qquad \ldots\ldots(1)$$

Now C, t and R are unknown, but it is reasonable to assume that t is proportional to the time T taken by the fibre to pass by way of the doffer from the cylinder to the sliver can, and the resistance R will be proportional to the yarn resistance $\bar{R}$ given in Figure 3. Then equation (1) can be written

$$\log_{10} Q = \log_{10} Q_0 - \frac{0{\cdot}434aT}{C.\,b\bar{R}} \qquad \ldots\ldots(2)$$

where a and b are constants of proportionality

which gives a relation $(\log_{10} Q_0 - \log_{10} Q)\bar{R} = \text{constant} = K$ ……(3)

K was evaluated from the experimental points for wool, Ardil, cellulose acetate and nylon and found to be constant for each fibre within the accuracy of measurement. The mean value of K was then used in equation (3) to calculate the full curves in Figure 2.

The fit of these calculated curves with the experimental points shows that the proposed explanation of the control of charge by leakage during the carding of fibres is in agreement with the available experimental facts in the case of wool, Ardil, cellulose acetate and nylon.

In the carding experiments T was kept constant so that, from equation (2), it would appear that the capacitance C of the "protein" group of fibres is not appreciably changed by variation of regain.

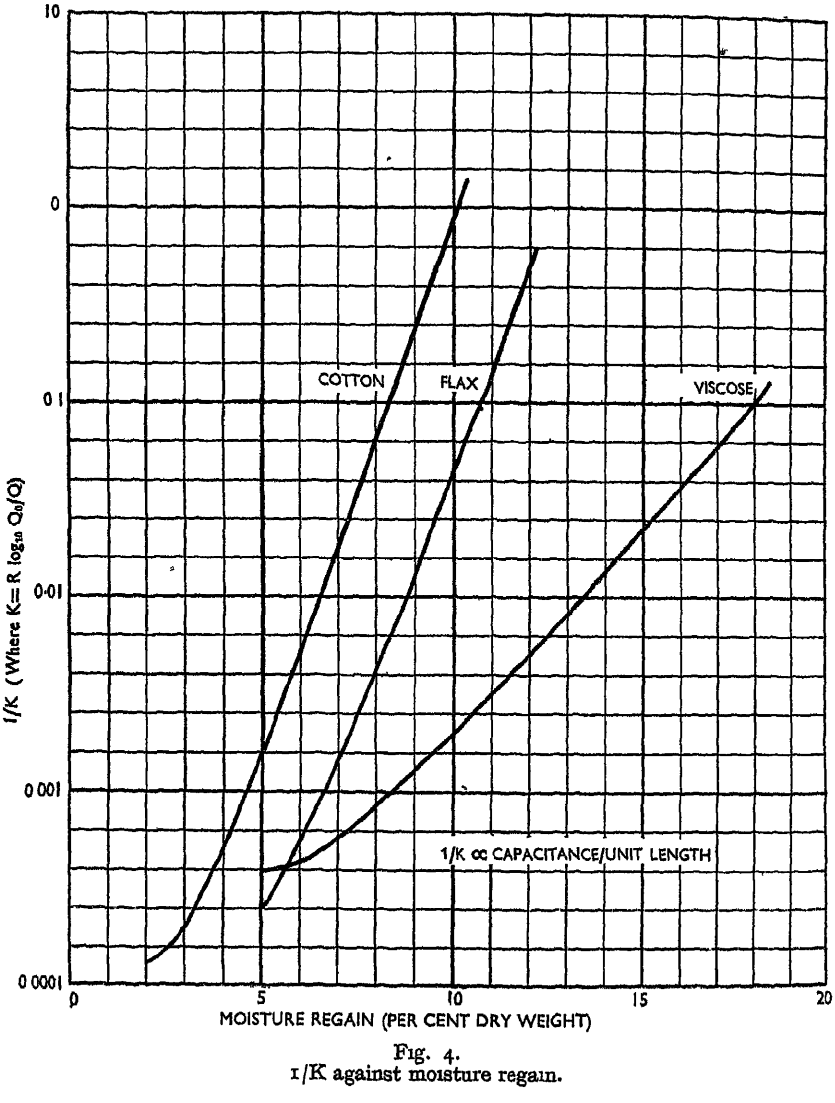

Fig. 4.
1/K against moisture regain.

When the same procedure is applied to the data for cotton, viscose and flax, no satisfactory fit can be obtained. The calculation is made less easy as a "maximum" charge is not obtained by experiment, but by extrapolation. It is found that $\bar{R}(\log_{10}Q_0 - \log_{10}Q)$ decreases continuously as the moisture regain increases; (the reciprocals of the calculated values are plotted in Figure 4). This variation would be found if the capacitance increased with increasing regain.

It may be noted that there is a critical leak resistance above which the charge lost by the fibre in passing from the cylinder to the sliver can will be insignificant. This resistance can be estimated on Figure 3 by determining on Figure 2 the regain at which the drop in charge rate first becomes apparent. These values are marked on Figure 3 by a vertical bar, and it will be seen that the four protein type fibres group together at a value of about 8×10^6 ohm.sq.cm./cm. The three cellulose fibres, cotton, flax and viscose, do not reach a limiting charge, even at regains as low as 2 per cent., but it is reasonable to assume that such a limiting charge would be reached if it is a function of the carding process and not of the fibre, provided that a sufficiently low regain could be obtained. The curves of Figure 2 for cotton, viscose and flax have been extrapolated to a value of charge of 0·018 microcoulombs per gram and the regains corresponding to this level are marked again with a vertical bar in Figure 3 All these resistance values are of the same order, 10^9 ohm sq.cm./cm , which is much higher than that for the protein type.

DISCUSSION

(*a*) *Electrical resistance of yarns.* The straight lines for nylon, acetate, Ardil and wool in Figure 3 are roughly parallel and are spaced along the moisture axis at distances roughly proportional to the moisture take-up of the fibres at normal relative humidities, as obtained from the known moisture relations of these fibres. Thus yarns of these four materials have roughly equal resistances at any given relative humidity over a considerable humidity range. This result is of considerable interest, as the fibre materials of nylon, acetate, Ardil and wool differ considerably, and indicates the great influence of the adsorbed water on the resistance of yarns.

Yarns of the three cellulose fibres, cotton, flax and viscose, form a similar grouping displaced along the moisture axis.

(*b*) *Level of electrostatic charge.* It has already been pointed out that the results in Table I and Figure 2 show that for nylon, acetate, Ardil, casein and wool, the charge measured on the sliver increases as the regain decreases until at moisture levels corresponding roughly to the moisture take-up of the fibres at 60-70 per cent. R.H., the static electrification tends to reach a steady value, roughly the same for all five fibres. Thus for these fibres it is to be expected that electrification would be present in carding up to 60-70 per cent. R.H., but that at higher humidity levels it would decrease very rapidly.

The cellulose fibres, cotton, flax and viscose, will normally develop considerably less static electrification than the protein fibres. At regains for these fibres corresponding to a relative humidity of 60-70 per cent., the charges developed are of the order of 5×10^{-5} microcoulombs per gram, compared with a figure of roughly 5×10^{-2} for the "protein" group—a difference of one thousand times. Not until the regains have reached a level corresponding to very low relative humidities of less than 10 per cent. do the charges on these cellulose fibres equal those developed on the protein fibres at 60-70 per cent. R.H It still remains to be proved whether the charge on cellulose fibres reaches a constant level at a sufficiently low regain.

It has been shown that, for the protein fibres, the experimental results for the variation of charge with regain are explained if the initial charge level is constant, independent of the regain, and the resistance of the fibre varies with the moisture Whether the initial charge level varies with the machine still remains to be proved.

The observation that the fibres tested divide into two distinct groups, and that the charge on the sliver is controlled by the regain of the fibre, indicates that the amount and nature of the adsorption of moisture by fibres is possibly of more importance as regards static electrification than the chemical constitution.

It is hoped to apply this technique to the study of the effectiveness of anti-static agents

It must be stressed again that this work is exploratory, dealing only with sliver from a cotton card, and that more detailed studies are necessary before further progress can be made.

The authors wish to acknowledge the assistance received from Mr. F. Dyke, whose practical experience of carding was essential in the carrying out of this work.

APPENDIX

The measurement of the Variation of the Resistance of Fibres with varying Moisture Regain

The measurement of the resistances of fibres at low moisture regains presents considerable experimental difficulty as the order of resistance to be measured may reach 10^{13} ohms This could be reduced by the use of short lengths or large diameters, but this expedient results in grave uncertainty in the corrections for the effects of the necessary metallic end clamps

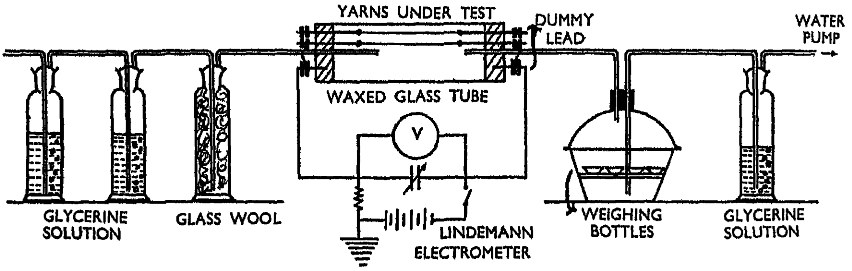

Fig 5.
Apparatus for measuring Resistance of yarns

The apparatus used is shown diagrammatically in Figure 5 Rovings of the fibres were prepared and twisted to about 3 twists per inch by hand, to give coarse yarns Details of these yarns are given in Table II A glass tube, 9 in. long and 3 5 in. diameter, was closed at both ends with stoppers through which brass rods were passed The yarns were held under slight tension by pairs of these rods, being fixed by chucks attached to the ends of the rods. The length of the yarns in the tube was about 4 in. To prevent leakage the internal and external surfaces of the tube and stoppers were coated with paraffin wax, a small clear window only being left for observation purposes. A small tube through each stopper allowed air to pass over the yarns By means of a water pump, air was sucked slowly through two bubblers containing aqueous glycerine solutions, then through a third bottle containing glass wool as a spray catcher, to the tube containing the yarns, after which the air passed through a vessel containing specimens of the fibres in weighing bottles, then through another bubbler containing glycerine solution to the pump. The humidity of the air passing over the yarns was controlled by the proportions of the water-glycerine mixtures, which were the same in all three bubblers for each reading

The resistances were measured by determining the rate of leakage of a condenser, the terminals of which were attached to the rods holding the yarns, each yarn being measured in turn. The air condenser of 1,000 $\mu\mu$F had a Lindemann electrometer permanently connected across its terminals. To make a reading the condenser was charged to 18 volts with a battery, and the time taken for a fall in voltage of 11·4 volts was measured with a stop watch. This time was of the order of 40 seconds. The natural leak of the apparatus was also determined for each set of readings by attaching the leads of the condenser to a pair of dummy leads through the stoppers, which were not connected by a yarn. The difference between the two rates of leakage enabled the conductivity of the yarn to be calculated.

To ensure that the yarns were in equilibrium with the air at each humidity level, readings were taken at intervals until a steady value was reached, when all seven conductivities were determined. The time taken to attain equilibrium was of the order of eight hours. Determinations were made with increasing relative humidities, so that the fibres would be under conditions of absorption in all cases. Experiment showed that it was necessary to made to control the temperature, but the room temperature was reasonably made to control the temperature, but the room temperature was reasonably constant at around 20° C.

Table II
Resistance of yarns at varying moisture regain

Material	Cross Section (sq. cm.) (A)	Length (cm.) (l)	$\bar{R}$, (ohms)						
Acetate	$4·1 \times 10^{-3}$	12·7	% Moisture	3·7	4·1	5·4	7·8		
			$\log_{10} (RA/l)$	7·77	7·64	7·26	6·74		
Ardil	$2·9 \times 10^{-3}$	14·2	% Moisture	8·6	9·1	10·4	11·0	13·8	
			$\log_{10} (RA/l)$	7·57	7·37	7·19	6·76	5·88	
Cotton	$4·5 \times 10^{-3}$	11·0	% Moisture	4·7	5·2	5·6	6·5	6·9	9·1
			$\log_{10} (RA/l)$	7·79	7·46	7·21	6·65	6·23	5·31
Flax	$7·0 \times 10^{-3}$	12·3	% Moisture	6·8	7·3	7·8	9·0	9·5	11·7
			$\log_{10} (RA/l)$	7·83	7·54	7·24	6·53	6·11	5·26
Nylon	$1·9 \times 10^{-3}$	11·0*	% Moisture	1·8	2·3	2·7	3·6	3·7	4·8
			$\log_{10} (RA/l)$	7·71	7·54	7·52	7·32	7·07	6·70
Viscose	$1·6 \times 10^{-3}$	10·8	% Moisture	8·8	9·9	10·3	11·6	12·4	16·9
			$\log_{10} (RA/l)$	7·53	7·44	7·25	7·02	6·57	5·55
Wool	$2·8 \times 10^{-3}$	10·7	% Moisture	9·5	10·6	12·3	13·0	17·1	
			$\log_{10} (RA/l)$	7·98	7·83	7·72	7·35	6·50	

The actual values of relative humidity were not determined, as it was considered that figures for the moisture regain of the yarns were of more value. These were determined on the samples of the seven fibres which were contained in open weighing bottles in the desiccator. Fresh samples were placed in these bottles at the beginning of each run, and at the end, after equilibrium of both resistance and regain had been attained and the conductivity readings taken, the vessel was quickly opened and the lids placed on the bottles, which were then quickly weighed and the regain found from the loss in weight after heating for four hours at 110° C. in an air oven.

The expression of the resistance of a material in the form of fine filaments of relatively short (*c.* 1·5 in.) staple length twisted into a coarse yarn of 10 cm. length is not simple. As, however, the filaments for all materials were of roughly the same length and of the same order of diameter, it was considered that comparative figures could be obtained by weighing the yarns, and from the known density of the material, calculating the equivalent cross sections of the yarn, all at a relative humidity of 65 per cent. The resistances were then expressed as ohms resistance per centimetre length for one square centimetre of cross sectional area. This, of course, neglects the difficult question of the area of contact between short filaments, especially when these filaments may be of varying cross sectional shape from the irregularities of cotton, viscose, and cellulose acetate to the smooth circular form of Ardil and nylon.

The results are given in Table II and are shown graphically in Figure 3, where the percentage moisture regain is plotted against the logarithm of the resistance in ohms per cm length for 1 sq. cm. of cross sectional area.

For each yarn the points lie roughly on a straight line, the resistance, of course, increasing with decreasing moisture regain. These lines are in the same order, and have much the same spacing, as the static electrification curves in Figure 2.

The only comparable figures for the resistance of yarns found in the literature were for wool and cotton (1), (2) and (3). The values given are in satisfactory agreement with those found in this work.

REFERENCES

[1] Murphy and Walker, *J Phys Chem.*, 1928, 32, 1761
[2] Walker, *J. Text Inst.*, 1933, 24, T145
[3] Walker, *Melliand*, 1930-31, 2, 93

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43—THE FINE STRUCTURE OF SISAL FIBRES

By R. D. Preston and Mavis Middlebrook

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Introduction

The interest of this laboratory has, for almost twenty years, largely centred on the molecular organisation of plant cell walls, and recently the opportunity was taken of examining sisal fibres, provided through the courtesy of Dr. P. Wilson, late of the Department of Textile Industries. While this investigation was undertaken primarily because this fibre presents points of particular botanical interest, these very peculiarities have enabled the presentation of an unusually clear picture of the architecture of the adult fibre. It is the purpose of this paper to describe briefly the structure thus revealed, in the hope it will prove of interest to fibre technologists not only as it applies to sisal itself, but also as it probably reflects the structure of native cellulose fibres generally. A more complete discussion, particularly of the botanical implications of the work will be given elsewhere in collaboration with Dr. Wilson.

The interest which attaches to sisal will perhaps be clear if we turn for a moment to the analogous case of structure determination of the wood in conifer trees. It should be emphasised first, perhaps, that in botanical nomenclature the term fibre refers to a single cell and not the fibre bundle of commerce. Since, however, this term is traditionally applied in technology to the commercial fibre we shall refer to the single units making up a fibrous material as "single cells". In wood the cells are long and narrow, with a cavity or lumen running the whole length of each cell exactly as in the case of fibrous cells—though here for clear reasons into which we need not go, they are called *tracheids* and not fibres. X-ray diagrams of such wood, or of single cells, show the presence of molecular chains of cellulose running in a single spiral round each cell,[3,5] and this is supported by observation of major extinction positions of single walls under the polarising microscope.[3,6] The same appears to be true in the case of hemp,[2] jute[4] and bamboo[7] fibres. Nevertheless there is the peculiarity that in thin transverse sections of wood, and to a smaller extent in hemp and jute but markedly in bamboo, the wall is optically heterogeneous Under the polarising microscope between crossed nicols, each cell is surrounded by an outer layer which is bright, while the bulk of the wall within it is dark or sometimes merely less bright, except for an innermost, very narrow layer which is again occasionally bright. It has proved particularly difficult to determine with any certainty the factors of structure underlying this heterogeneity largely on account of difficulties inherent in the close proximity of the layers, but this has at last been achieved [10] It appears that the dark layer, as was in fact known before,[5] is the one giving rise to the X-ray diagram and is composed of cellulose chains lying in a fairly steep spiral. In the bright layers, however, the cellulose spiral is much less steep and the "micelles" are dispersed about their mean direction through an angle which is much larger than that in the inner layer. Since fibres generally present the same optical phenomena, it seems reasonable to assume that their structure may be similar and it was with this in mind that the work on sisal was undertaken. The particular interest in sisal fibres is that, owing to their remarkably slow growth, developing fibres are available in quantity, and it could therefore be expected that, if their structure is indeed of the type suggested above, then the outer layer could be examined alone and without the complications ensuing from the presence of other layers. This has turned out to be the case and this direct demonstration forms, therefore, a valuable check on the interpretation following indirect evidence used with wood and bamboo.

While this is clearly not the occasion to enlarge on the botanical interest in sisal, some of the salient morphological features will be of value to an understanding of the structures later revealed. The material consists of fibres which are themselves composed of single cells closely cemented together. Each cell originates as a small, isodiametric blob of protoplasm surrounded by a thin, delicate sheath of cellulose and pectin, the primary wall with which we shall not be directly concerned. It develops into a fibrous cell by enormous elongation, with very little relative change in girth, and during the whole of this elongation the wall remains thin. After elongation has ceased, the cell wall becomes gradually thicker by the apposition inside the primary wall of secondary layers of cellulose, and finally the whole wall lignifies and the cell contents die, leaving a liquid-filled cavity running down the centre of the cell. In transverse section the wall shows exactly the phenomenon seen in wood and in other fibrous cells. Here, however, the deposition of the secondary layer occurs so slowly (taking months instead of the two days of wood) that material is readily available containing cells with the outer layer only. Further, since in sisal, as in other monocotyledons, the growing zone of the leaf continues active at the leaf base during the life of the plant, then on proceeding from the base to the tip of the leaf we are passing through zones of cells which are more and more mature The choice of any particular stage of development involves therefore nothing more than the choice of the corresponding level in the leaf.

Material and Methods

The material available was in the form of the complete fibre system of retted young and mature leaves Since the base of a sisal leaf is still thin-walled and growing, it naturally follows that during commercial preparation of the fibres these thin-walled cells, which are potential fibres, have been removed along with other thin-walled tissues, in consequence the fibre system is always some 10 cm. shorter than the fresh leaf from which it was prepared. In locating the level at which material was chosen, therefore, distances along the leaf are measured from the base of the retted fibre system and not from the leaf base itself. Specimens were chosen from three levels in a young and two levels in a mature leaf showing different stages of thickening of the cell wall. X-ray diagrams were obtained of parallel bundles of fibres using the CuKα radiation from a Shearer tube collimated by a slit 0 5 mm. diameter and using a flat film. Major extinction positions of the fibre wall in surface view were determined in the usual way[3] under a Lietz polarising microscope, and birefringences in transverse section were calculated from the phase differences, measured by means of a de Sénarmont compensator, and section thickness; this latter factor being in turn determined by forcing a few cells of a section on their sides and using a Leitz Okular-schraubenmikrometer. Cell length measurements were made on material macerated by alternate treatment with 5 per cent. KOH and chlorine water until the cells fell apart on shaking. These were stained with Congo Red and the lengths of straight cells measured by projection on to a large screen. As with other fibres it is essential for a demonstration of optical heterogeneity that the section thickness shall be as near 5μ as possible, and certainly not greater than 10μ. Correspondingly, sections of this material were cut on a microtome after embedding in (not merely covering by) celloidin.

Table I. Fibre length and chain orientation in sisal fibres.

Leaf	Length of Leaf	Distance from Base	FIBRE LENGTH†			MAJOR EXTINCTION POSITION†			Angle of pits	Angle from X-ray Data	Percentage Cellulose
			Number of Observations	Range (mm)	Mean* (mm.)	Number of Observations	Range	Mean*			
B 3	153 cm	0– 3 cm.	359	0·33–2·68	1·06±0 34					49°	65·4
,,		54–58 cm.	158	1·15–5 15	2 58±0 78					18°	78 3
C.105	79 9	0– 3 cm	165	1 23–5·16	2·78±0·82	31	26 4–64°	40 2±8 4°	39 5°	40°	77 3
,,		10–13 cm	181	1 27–4·96	2·78±0 89	31	8·0–32 3°	20 4±7·2°		18°	83 2
,,		76–79 9 cm.	267	0 87–4·92	2 50±0 94					20°	83 2

* The errors given are the standard errors (*i.e* (standard deviation)/$\sqrt{n}$).

† The angles given throughout are those made to the *length* of the fibre.

Table II. Wall thickness and birefringence in sisal fibres. (Leaf C 106 is closely similar to leaf C 105 in Table I.)

Leaf	Length of Leaf	Distance from Base	Number of Observations	WALL THICKNESS IN μ			BIREFRINGENCE OUTER LAYER			BIREFRINGENCE INNER LAYER		
				Total	Outer Layer	Inner Layer (By difference)	Number of Observations	Range	Mean	Number of Observations	Range	Mean
C.106	74 2 cm	1 cm.	30	0 68±0·15	0·68±0 15	0·00	30	0·0102–0 0237	0 016			
C 106	,,	12 cm.	33	1·26±0 11	0·66±0·18	0·60	22	0 0087–0·0191	0·015	22	0 0044–0 0078	0 0064

Results

Photomicrographs of adult fibres in transverse section are presented in Plate I, Fig. 1 (a) and (b). These represent the same section taken by unpolarised light (Fig. 1a) and in polarised light between crossed nicols (Fig. 1b). It will be noted that although the cell lumina are unusually large for fibrous cells the walls are nevertheless heavily thickened, and the bulk of this thickening layer is dark between crossed nicols. Only a thin outer layer around each cell is bright and therefore strongly birefringent, when viewed in this way. Dried fibrous material of this kind is not easy to cut and it was found necessary during the investigation to use all the material which had been cut satisfactorily. The sections illustrated in the Plate are therefore somewhat inferior and perhaps do not at first sight display any too well the features involved here. Fig. 1 is therefore drawn to show the condition more clearly, and reference from this figure to the photograph in Plate I, Fig. 1(b) will then make the position clear. In longitudinal section (Plate I, Fig. 3) on the other hand, the bulk of the wall is bright, so that this thick inner layer presumably consists of cellulose "micelles" arranged nearly parallel to the length of the cells. The presence of "micelles" arranged in such a steep spiral is in fact clearly indicated in the X-ray diagram of fibres from the same level in the leaf (Plate I, Fig. 2). In point of fact it is not possible from the X-ray photograph alone to determine whether the "micelles" have a preferred orientation parallel to the cell length about which there is considerable angular dispersion, or whether they lie in a spiral. Comparison with other cell types, however, leads us to suspect that the micelles do lie in a spiral, and the spread of the lateral arcs would indicate that the angle between the micelles and the cell length is about 18° (Table I). This is supported by determinations of the major extinction position (Table I). It is important to note, however, that if the cell wall consisted throughout of micelles inclined at about the same angle, then the angles determined in the two ways should be equal. Although the spiral angle determined from the X-ray diagram is unavoidably a rough approximation only, the discrepancy does suggest that the wall is not indeed homogeneous.

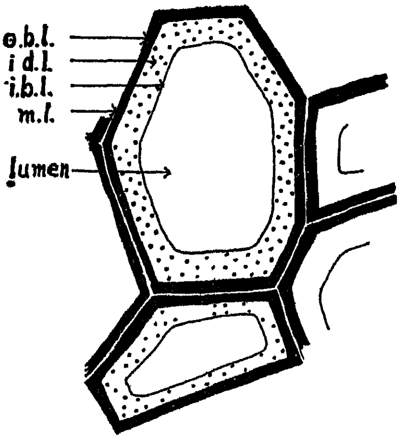

Fig. 1

We turn now, therefore, to the less mature fibres lower down the leaf, where the wall is thinner (Table II) and the inner layer has not yet been deposited (Plate II, Figs. 1a and b) Here the outer bright layer can be studied alone. It should be remembered that, had this leaf been allowed to develop, the cells here would eventually have laid down the thick inner layer. Unless, therefore, there is some difference associated with the age of the leaf, this outer layer is strictly comparable with the outer layer in the adult cells observed above, whose features could not be determined on account of the masking effect of the inner layer. That the outer layer is structurally identical in the two cases is indicated by the close similarity of their birefringences in transverse section, of an order quite different from that of the inner layer (Table II). The X-ray diagram of a bundle of cells from this younger region is, however, quite different (Plate II, Fig. 2). Now the micelles are clearly arranged in a spiral much flatter than that determined above, whose angle to the cell length can be deduced[5] as about 40°. This figure compares favourably with that determined optically by the major extinction position, and the run of the mouths of the slit pits* (which are visible here but become occluded on the deposition of the central layer) (Table I). Since the average lengths of the cells in the two positions are not significantly different (Table I) there is no possibility here that this difference in spiral angle is associated with a length difference in the way recently demonstrated[6] in wood cells. The conclusion is inevitable therefore that in the fully grown fibre there is an outer enveloping layer in which the cellulose micelles lie along a spiral much flatter than that in the rest of the wall

It may be noted in passing that with the two series of cells covered by outer layer only, the shorter celled tissue (B.3, 0-3 cm., Table I) shows rather flatter spirals (Plate II, Fig. 3) than the longer celled tissue (C 105, 0-3 cm., Table II) This is a further example of a connection, which is possibly quite general, of cell dimensions with structure.[6]

Discussion

In commenting upon these results it must be admitted at the outset that the structure thus envisaged is not a novel conception in fibres It was in fact suggested a number of years ago[9] that fibres are generally built on this plan. The importance of the present work, however, lies in the fact that this is only the third time this type of structure has been demonstrated in fibrous cells by strictly crystallographic means, the other two cases being wood fibres[10] and bamboo[7], and the first case in which the features of the outer layer have been demonstrated unequivocally in tissues where the complexities, due to a central layer within, are absent. It is, moreover, now possible to deduce other features of interest concerning the structural peculiarities of these two wall layers. Optically each layer is built up of two rather ill-defined fractions; a fraction which is intrinsically birefringent, and the rest of the wall material which is isotropic. These may not correspond, even roughly, to the familiar crystalline and non-crystalline fractions determined by X-ray methods, since extra-micellar chains which lie parallel will contribute to the birefringence. The birefringent fraction will consist entirely of cellulose while the rest will comprise the non-birefringent cellulose fraction plus lignin and other incrusting materials, all of which are non-birefringent. Now in sisal, chemical analysis at the 12 cm. level shows the wall to contain 83 per cent.* by weight of cellulose (Table I) and ignoring for the moment a small correction for density this may be taken also as the volume percentage. If a volume fraction f of this cellulose is crystalline in the present sense, then the partial volume of the wall associated with crystalline cellulose is $f\ (0{\cdot}83)$. Similarly the non-crystalline cellulose has a relative volume of $(1-f)\ (0{\cdot}83)$ and the incrusting substances $(0{\cdot}17)$. If, now, we assume that the refractive indices of this composite wall can be determined, from these fractions and the corresponding refractive indices, by the mixed formulæ commonly used for liquids[1] then, taking the refractive indices as determined in transverse section of the wall, we may set up the equations

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* Pits in a wall are small circular areas in which wall thickening has not occured, so that canals are left running through the wall Commonly the secondary wall layers overarch the pit areas so that the pit mouth becomes smaller towards the lumen In sisal, as in many other fibres the (circular) mouth becomes elongated, as seen in surface view, into a slit and hence these are called slit pits. The slit mouth of these pits lies parallel to the cellulose chain direction.

$$n_\gamma' = f\,(0{\cdot}83)n^\theta_{\gamma_{cr}} + (1-f)(0{\cdot}83)n_c + (0{\cdot}17)n_r \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$n_a' = f\,(0{\cdot}83)n^\theta_{a_{cr}} + (1-f)(0{\cdot}83)n_c + (0{\cdot}17)n_r \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Whence

$$n_\gamma' - n_a' = f\,(0{\cdot}83)(n^\theta_{\gamma_{cr}} - n^\theta_{a_{cr}}) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where n_γ' and n_a' are the major and minor refractive indices observed in transverse section (and $n_\gamma' - n_a'$ therefore is the birefringence) $n^\theta_{\gamma_{cr}}$ and $n^\theta_{a_{cr}}$ are the corresponding refractive indices of crystalline cellulose when the direction of propagation makes an angle θ with the chain length, n_c is the refractive index of the non-crystalline cellulose, and n_r that of encrusting substances.

Transposing (3) we have

$$f = \frac{(n_\gamma' - n_a')}{(0{\cdot}83)(n^\theta_{\gamma_{cr}} - n^\theta_{a_{cr}})}$$

If we assume further that the percentage of cellulose determined by chemical analysis applies to each layer individually at the 12 cm. level (see below) and that no very marked angular dispersion occurs, we can take the refractive indices of cellulose to be $n_\gamma = 1{\cdot}60$ and $n_a = 1{\cdot}53$ (*i.e.* the indices parallel and perpendicular to the length of cellulose chains) and we can then use this relation to calculate f for each layer in turn. $n^\theta_{\gamma_{cr}}$ may be calculated from n_γ *and* n_a in the usual way. The method will be clear from Fig. 2. A B C D E F represents a piece of the wall of a sisal fibre, A B C D being a transverse face and C B E F a tangential longitudinal one. The n_γ direction is taken to lie at an angle θ to the length of the cell, B F, along which light is propagated. The refractive indices in transverse section then correspond to the projection of the ellipsoid of rotation with axes n_γ and n_a —the index ellipsoid—upon the transverse face. Clearly $n^\theta_{a_{cr}} = n_a$ and it remains only to calculate $n^\theta_{\gamma_{cr}}$, the major axis of the projection ellipse. This can readily be done since, as will be clear from the figure, the following relation obtains:—

$$\frac{(n^\theta_{\gamma_{cr}})^2 \sin^2\theta}{n_\gamma^2} + \frac{(n^\theta_{\gamma_{cr}})^2 \cos^2\theta}{n_a^2} = 1$$

whence

$$(n^\theta_{\gamma_{cr}})^2 = \frac{n_\gamma^2\, n_a^2}{n_\gamma^2 - (n_\gamma^2 - n_a^2)\sin^2\theta}$$

For the outer layer $\theta = 40°$, $n^\theta_{\gamma_{cr}} = 1{\cdot}56$. Hence

$$f = \frac{0{\cdot}015}{(0{\cdot}83)(0{\cdot}03)} = 0{\cdot}6$$

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* We are indebted to Miss Jagger of the Department of Textile Industries for the chemical analyses of the material.

i.e. the cellulose is 60 per cent crystalline. At the 1 cm. level f would be

$$\frac{0{\cdot}016}{(0{\cdot}77)(0{\cdot}03)} = 0{\cdot}69$$

i.e. 69 per cent., so that the correct figure at the 12 cm. level probably lies between 60 and 69 per cent. This is of the order found by Hermans for native fibres.

In the central layer, however ($\theta = 18°$, $n^{\theta}_{\gamma_{cr}} = 1{\cdot}538$)

$$f = \frac{0{\cdot}0064}{(0{\cdot}83)(0{\cdot}008)} = 0{\cdot}96$$

This would seem an absurdly high figure, indicating as it does that 96 per cent. of the cellulose chains lie strictly parallel, although not all can be considered to lie within the regular spatial arrangement of the micelles It is certainly an over-estimate for several reasons, one being a probable subjective error in measuring the low birefringence—the natural tendency being to overweigh the larger birefringences Comparison of the two figures does, however, show that there is a difference between the wall layers in addition to the general tilt of the cellulose micelles. It is to be noted that the correction for density which should be made in the above calculations will have no effect on the relative values of the fraction f; each will merely be multiplied by a factor of the order $1{\cdot}53/1{\cdot}46$. Either the percentage of crystalline cellulose is in fact different, or if it is the same, then the angular dispersion of the micelles in one layer is much greater than in the other The real condition may of course be intermediate, but for the moment this factor may perhaps best be interpreted as an orientation factor.[1]

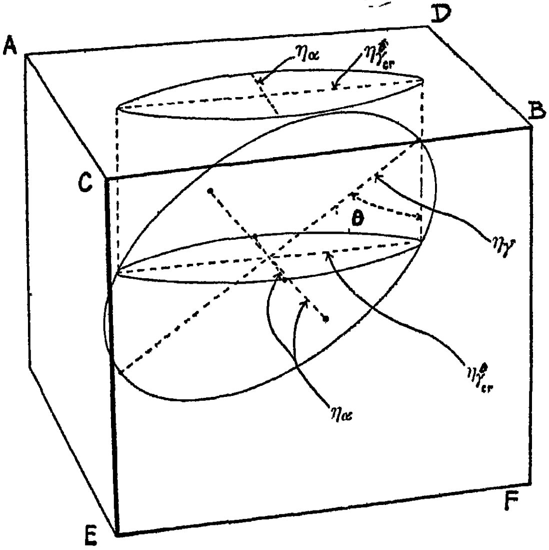

Fig 2

It seems to the writers, however, that interpretation of the factor f should be approached with extreme caution. In the present case where the cellulose chains are steeply inclined, increase in angular dispersion probably leads to a higher value of birefringence in transverse sections and a high value of f may therefore be associated with considerable disorientation. In other words the factor f could be interpreted strictly as an orientation factor only if the birefringence were measured *exactly* in the plane of the preferred orientation. In point of fact, however, the X-ray diagram does not suggest that the observed difference in f is due to angular dispersion alone (for it is to be remembered that the bulk of the spread of the arcs is to be attributed to the spiral organisation of the cells and not to angular dispersion proper), and it seems very possible that many of the extra-micellar chains do lie parallel. This is a point to be examined at a later stage.

One final point seems worthy of attention at this time since it sheds some further light on these aspects of wall structure. Although the X-ray diagram of immature fibres shows the lateral arcs rather intense, if somewhat spread, that of the mature fibres, which one might expect to correspond to the diagrams of outer and central layers superposed, refers on the other hand almost exclusively to the central layer with only faint indication of wider arcs which would correspond to the outer layer. It seems therefore very probable that during or after the deposition of the second layer the organisation of the outer layer undergoes such a change as to reduce the intensity of the X-ray reflections. This could be an increase in the angular dispersion of the micelles caused by the slight swelling concomitant with lignin deposition or development such as has been noticed in the very similar case of hemp fibres[2] and mentioned also with other tissues. The fact that the birefringence in transverse section is almost identical in young and mature fibres cannot be regarded as weighing against this possibility since angular dispersion might have little effect in the precise circumstances obtaining in the outer layer.

It seems, therefore, that in sisal the outer layer in the wall differs from the inner layer in at least two respects. First, in the outer layer the cellulose micelles are inclined in a spiral which makes an angle of some 40° to the length of the cells, whereas in the central layer the angle is of the order of 20°. Secondly, while the angular dispersion of the micelles in the outer layer about their common direction is probably very considerable, the micelles in the central layer are certainly oriented more nearly parallel to each other—and possibly even the chains in the intermicellar regions are oriented less at random—the structure in this respect therefore resembling closely that in ramie. The surfaces of the cells are therefore very different structurally from the rest of the wall within and it seems highly probable that the same is true of many other fibre types.

SUMMARY

The slow growth of sisal fibres makes them very favourable material on which to study the structural peculiarities of different layers in the wall. In this preliminary investigation it is shown, without any doubt, that the narrow, first formed outer layer of the cell wall differs from the bulk of the wall within in that the cellulose micelles there lie in a spiral making an angle of about 40° with the cell length, whereas in the inner layer the angle is about 20°. It is further probable that the micelles in the outer layer are dispersed about their common direction much more than are those in the inner layer. The surface of the fibres is therefore structurally different from the bulk of the wall within and the same is probably true for many other fibrous cells.

REFERENCES

[1] Hermans, P. H. 1946. *Contributions to the physics of cellulose fibres.* Amsterdam.
[2] Kundu, B. C. and Preston, R. D. *Proc. Roy Soc*, 1940, B128, 214
[3] Preston, R D *Phil Trans.*, 1934, B224, 131.
[4] Preston, R D. *Proc. Roy. Soc.*, 1941, B130, 103.
[5] Preston, R D *Proc. Roy. Soc.*, 1946, B133, 327.
[6] Preston, R. D. *Proc Roy Soc.*, 1947, B134, 202
[7] Preston, R D and Singh, K. *Unpublished.*
[8] Preston, R D *Biochim. et Biophys. Acta*, 1948, 2, 370.
[9] Steinbrinck, H. *Naturwiss*, 1927, 15, 978.
[10] Wardrop, A. B. and Preston, R. D. *Nature.* 1947. 190, 911.

Department of Botany, The University of Leeds.

PLATE I

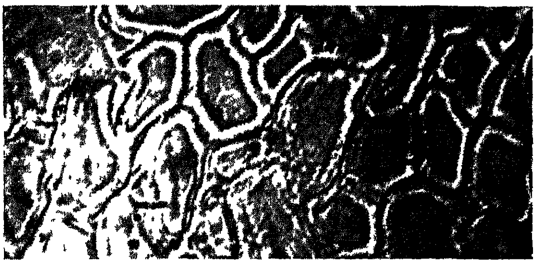

Fig 1a

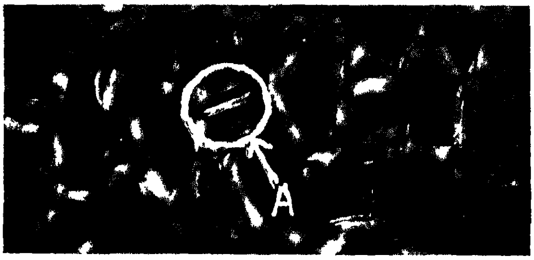

Fig 1b

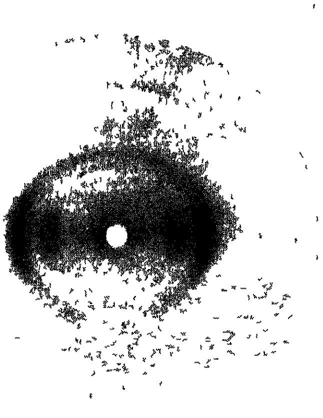

Fig 2

PLATE I

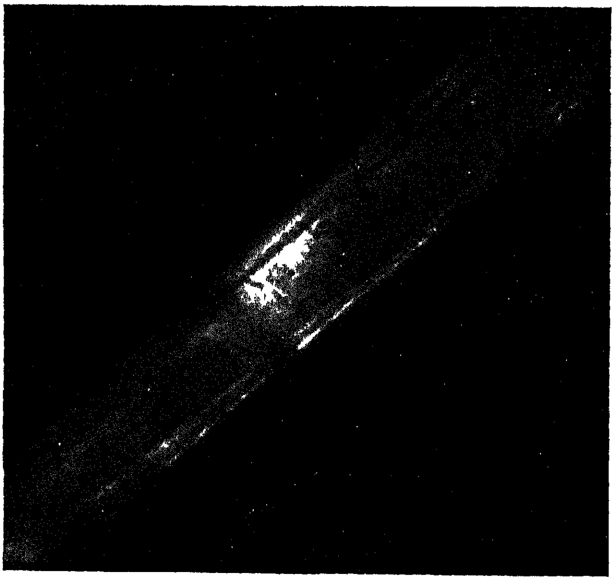

Fig 3

PLATE II

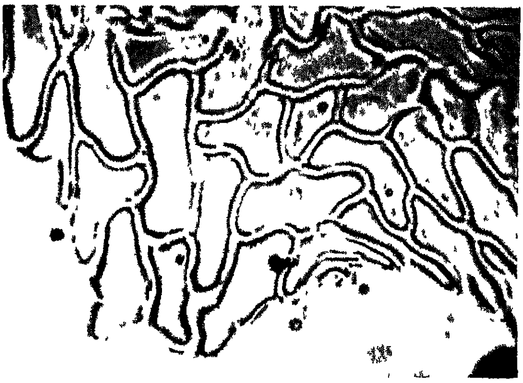

Fig 1a

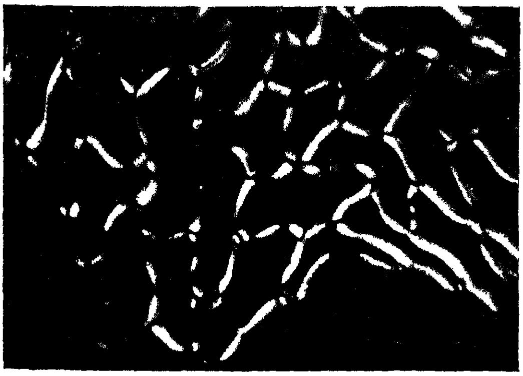

Fig 1b

PLATE II

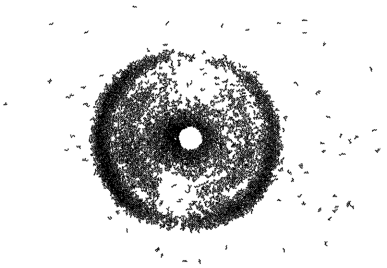

Fig 2

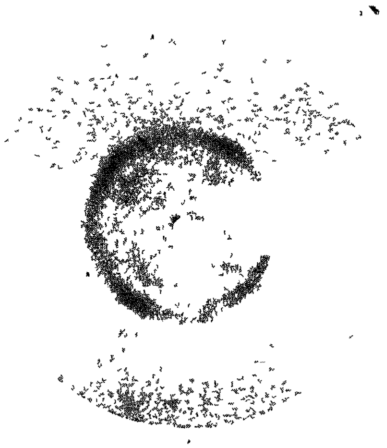

Fig 3

44—FURTHER ANALYSES OF AUSTRALIAN FLEECE WOOLS

By R. B. SWEETTEN

(*Copyright by the Textile Institute*)

Lipson and Black (1944) presented data showing the variations in the amounts of wax, suint, dirt, moisture and wool, found in some 200 samples of greasy wools grown chiefly in New South Wales. In this laboratory 150 samples of greasy fleece wools, all substantially free from vegetable matter, have been analysed, using the following method. Representative samples for analysis, weighing usually 15-25 grams, were drawn from larger samples weighing 6-8 lb. The latter were, in turn, representative of lots of wool offered for appraisement in the wool-brokers' stores* The samples for analysis were shown to be representative of the lots from which they were drawn by comparing the oven-dry yields of clean wool in these small samples, with those obtained by scouring larger samples in the Testing House. The wax content was determined by four hours extraction with re-distilled petroleum ether, while the suint content was estimated by subsequent extraction with cold distilled water. The suint solution was filtered prior to evaporation The dirt remaining in the wool after removal of the wax and suint was determined by weighing the oven-dry wool before and after a mild soap and soda-ash scour. The loss in weight of the wool, together with the weight of the dry residue collected by filtering the suint solution, gave the total dirt content of the sample. The moisture content of the original wool was determined by drawing another small sample at the same time and drying this for four hours at 100-105° C The method is identical with that used by Lipson and Black (1944), and is basically the same as that described by Freney (1940).

Most of the samples analysed were from Victoria and South Australia, but some from every state except Queensland were examined. The wools came from the 1942-3, 1943-4 and 1944-5 clips. Apart from one sample each of Lincoln and Southdown wool, all were of merino, crossbred, full fleece and lamb types. Merino wools included those of 64s quality and finer, also those of 58s to 64s quality having merino characteristics and 92 such samples were analysed Crossbred wools included those of 64s to 58s quality, having crossbred characteristics, and stronger wools, but not including Downs, Shropshire and Lincoln wools. Forty-five such wools were analysed. Eleven lambs wools were analysed and these included lambs wools of all qualities.

In Tables I and II the complete data are presented for those samples in which extreme values of the different constituents were found, together with the average values for merino, crossbred and lambs wools, and the results for the single samples of Southdown and Lincoln wools.† When the figures for moisture content are being considered, it should be borne in mind that the samples were exposed to the atmosphere in the Testing House for varying period prior to analysis.

The ranges for the amounts of the constituents present in the fleece samples are, in general, somewhat wider than those recorded by Lipson and Black. This may be due to the selection of samples examined, for all were

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* The quantities of wool represented by the samples ranged from 1 to 27 bales, and averaged 6 bales

† Values of less than 5% have been reported to the nearest 0·1%, values between 5 and 15% to the nearest 0 2%, and values over 15% to the nearest 0·5%.

Table I

Details of Analyses of Samples showing the Extreme and the Average Values for Fleece Constituents. Results expressed as Percentages of the Weight of the Greasy Samples.

Sample No	Class of Wool	District of Origin	Wax	Suint	Dirt	Moisture	Oven Dry Wool	Wool Quality	Length of Wool
7211	Merino	Hay, N S W.	3·9*	1·8*	48·0*	9·0	36·5*	64s up	Short
6730	,,	Nile, Tas	36·5*	7·0	10·0	9·2	37·5	74s up	Short
7569	,,	North West, W A	14·0	12·8*	20·0	11·4	41·0	64/70s	Medium
5654	,,	Casterton, Vic ...	18·5	5·4	5·4*	9·2	60·0	64s up	Short
5598	,,	Broken Hill, N S W	12·4	7·6	31·0	7·2*	40·5	64/60s	Good to Medium
7438	,,	Eastern Goldfields, W.A	17·5	8·0	12·2	14·0*	48·0	70s up	Good to Medium
1534	,,	Skipton, Vic	12·8	5·2	6·0	8·8	66·5*	64/60s	Good
		AVERAGE VALUES	15·0	5·8	16·0	10·0	52·5		
7027	Crossbred	Wycheproof, Vic	2·1*	2·8*	23·5	10·8	60·5	56/58s	Good to Medium
1830	,,	Chatsworth, Vic	19·0*	6·8	10·0	11·8	53·0	60s	Good
7129	,,	Goulburn Valley, Vic	7·6	13·0*	7·4	17·0*	54·5	56s	Good to Medium
5371	,,	Conara, Tas	13·4	5·2	4·0*	11·6	65·5	60s	Good
2291	,,	N E Coast, Tas	7·8	5·2	35·0*	8·2	42·5	58s	Good
2439	,,	Outalpa, S A	10·8	4·4	34·0	7·8*	41·5*	58/60s	Good
646	,,	Mortlake, Vic.	9·0	4·4	5·6	11·4	69·5*	56/50s	Good
		AVERAGE VALUES	12·0	6·8	11·4	11·0	58·0		
6620	Lambs	Willow Grove, Vic	6·4*	7·2*	4·2	13·0	68·0*	50/56s	Good
2580	,,	Horsham, Vic.	23·5*	5·0	7·2	10·6	54·0*	60/64s	Good
476	,,	Buckley, Vic	19·0	3·4*	8·0	9·0*	59·5	64s up	Medium
6619	,,	Tantanoola, S A.	17·0	5·2	3·8*	11·4	61·5	56/58s	Good
2560	,,	Woodside, Vic .	16·0	5·4	10·0*	11·4	56·5	58/60s	Medium
2979	,,	Officer, Vic.	15·0	6·6	6·8	14·2*	56·5	56/58s	Good
		AVERAGE VALUES	16·0	5·4	6·4	11·2	60·5		
2371	Lincoln	Hawkesdale, Vic	6·6	3·5	2·3	12·2	74·5	32/36s	Good
891	Downs	Edenhope, Vic	14·8	10·8	10·6	13·4	50·5	58/60s	Good

* Indicates extreme values for the various constituents

Table II

Details of Analyses of Samples showing the Extreme and the Average Values for Fleece Constituents. Results expressed as Percentages of the Weight of Oven-dry Wool in the Sample.

Sample No	Class of Wool	District of Origin	Wax	Suint	Dirt	Moisture	Wool Quality	Length of Wool
7211	Merino	Hay, N S W	10·6*	4·9	133·0*	25·0	64s up	Short
6730	,,	Nile, Tas	96·5*	18·5	26·5	24·5	74s up	Short
325	,,	Trawalla, Vic	26·0	3·6*	16·0	—	80s up	Good
7569	,,	North West, W. A	34·5	31·5*	49·0	28·0	64/70s	Medium
5654	,,	Casterton, Vic.	31·0	9·2	8·8*	15·5	64/60s	Medium
8234	,,	Trawalla, Vic	28·0	6·8	15·0	12·8*	64s	Good
7393	,,	North West, W A	23·0	20·5	69·0	32·0*	70s up	Medium
		Average Values	29·5	11·4	33·5	19·5		
7027	Crossbred	Wycheproof, Vic.	3·5*	4·6*	38·5	18·0	56/58s	Good to Medium
1830	,,	Chatsworth, Vic.	35·5*	13·0	19·0	22·0	60s	Good
4012	,,	Wakool, N S W	18·5	25·0*	37·0	24·0	56s	Good
5371	,,	Conara, Tas	20·5	7·8	6·0*	17·5	60s	Good
2439	,,	Outalpa, S. A.	26·0	10·6	82·5*	19·0	58/60s	Good
1216	,,	Nile, Tas	24·5	7·6	10·0	13·6*	58/56s	Good
7129	,,	Goulburn Valley, Vic	14·0	23·5	13·4	31·5*	56s	Good to Medium
		Average Values	21·0	12·0	21·5	19·5		
6620	Lambs	Willowgrove, Vic.	9·4*	10·6	6·2*	19·0	50/56s	Good
2580	,,	Horsham, Vic	43·5*	9·4	13·4	19·5	60/64s	Good
476	,,	Buckley, Vic.	32·0	5·8*	13·4	15·0*	64s up	Medium
2979	,,	Officer, Vic.	26·5	11·8*	12·0	25·0*	56/58s	Good
2560	,,	Woodside, Vic.	28·5	9·4	18·0*	20·0	58/60s	Medium
		Average Values	27·0	9·0	10·8	18·5		
2371	Lincoln	Hawkesdale, Vic.	8·8	4·6	3·0	16·5	32/36s	Good
891	Downs	Edenhope, Vic.	29·0	21·0	21·0	27·0	58/60s	Good

* Indicates extreme values for the various constituents.

considered to be unusual wools. Thus, merino sample 7211 and crossbred 7027, containing the lowest percentages of wax and suint, were described by wool appraisers as "dry" wools, and it may be noted that these differ widely in the amount of wool present and are not at all abnormal as regards moisture. However, merino sample 6730, on which the highest value for wax and suint was obtained, appeared very greasy when handled, being described by wool appraisers as "fatty". It is apparent that the term "dry" as applied to the wool in this sense implies a low percentage of wax present and its antithesis is not necessarily "damp" but may be "fatty" or, as has been shown by Lipson and Black (1944), "oily". In wools of more normal appearance the highest value for wax was 21·0 per cent. for merino wool and the lowest values recorded for wax and suint were 7·4 per cent. and 2·2 per cent. respectively, for merino wools, and 7·0 per cent. and 4·4 per cent. respectively for crossbred wools.

In view of the special selection of some of the samples, which in the opinion of the appraisement staff needed thorough analysis to explain apparently abnormal features, the average figure for each constituent is of doubtful significance. However, it may be worth noting that the differences between the various average figures for merino wools and crossbred wools are not as marked as the differences noted by Lipson and Black (1944).

The figures obtained in these analyses represent the average values for the different constituents in at least several hundred pounds of wool. More extreme values for wax, suint, dirt and wool, found in small specially selected samples of fleece wools are set out in Table III.

Table III
Details of Analyses of Specially Selected Samples of Fleece Wools

Sample			Constituents			
		Wax	Suint	Dirt	Moisture	Wool
Basal third of staples from very "fatty" black-tipped wool Merino 60/64s quality, 2½ to 3½ ins long.	*A	42 0	4·6	3 0	8·6	43·5
	*B	97 0	10·6	7·0	20·5	—
Distal third of staples from Crossbred wool, 56s quality, 4 to 5 ins. long. Distal half of staples from this wool were very "dry."	*A	0 5	1·3	5·8	11·8	80 5
	*B	0 6	1·6	7 2	14·5	—

*A Calculated as percentages by weight of the greasy sample.
*B Calculated as percentages of the weight of oven-dry wool in the sample.

ACKNOWLEDGEMENTS

This work was carried out at the Melbourne Testing House of the Australian Wool Realisation Commission, to whom acknowledgement is made for permission to publish this paper. I am indebted to Dr. R. H. Watson, Officer-in-Charge, Australian Wool Realisation Commission Testing House, for advice and criticism during both the experimental work and the preparation of the manuscript, and to those other members of the staff of the Testing House, who assisted me by selection or analysis of samples reviewed.

REFERENCES

Lipson, M. and Black, U A. F. *J. & Proc. Roy. Soc. N S.W* , 1944 78, 84
Freney, M. R. *Council Sci and Ind Res* (*Australia*), 1940, Bull 130

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Letters to the Editor

[*The Institute is not responsible for the opinions of correspondents.*]

To the Editor, *Journal of the Textile Institute.*

EFFECT OF GILLING ON THE STRENGTH OF WOOLLEN YARNS

Recently an experiment has been made to determine the effect of introducing a gilling process on the strength and appearance of woollen spun yarns. A quantity of 64s Australian wool was made into a woollen yarn by passing it through a woollen card consisting of a three part scribbler, two part carder and tape condenser, and a woollen mule. The sliver was condensed to 11 skeins and spun to 14s Yorkshire Skeins Woollen with approximately 5 turns per inch. A further quantity of the same wool was then passed through the scribbler at the same rate of production but instead of going directly forward to the carder the sliver was passed six times through an intersector gill box; 4 ends up, with a draft of four, to align the fibres in a more parallel order. The gilled sliver was then fed to the two-part carder by allowing it to pass from a can through the normal traversing shuttle of the scotch feed. This method of feeding meant that the fibres actually entered the card at right angles to their direction of movement on the feed sheet, but to have fed by any other means would have been far too complicated. It was quite apparent from the wool on the workers of the carder that the fibres were very quickly re-orientated in the direction of movement through the card. The sliver was condensed and spun to the same count as before.

In comparing the resultant yarns it was evident that the increased alignment of the fibres resulted in a more uniform splitting between the tapes for the yarns made from the gilled wool were far more uniform and less hairy than the normal woollen yarns, in fact they might almost be called pseudo-worsted yarns. Besides imparting a more uniform appearance to the yarns the gilling operation was also apparently responsible for some 23 per cent. increase in yarn strength. Details are given in the accompanying table.

	Normal Woollen Process	Extra Gilling
Count (Yorkshire Skeins Woollen)	14·4	14·2
Turns per inch	5·3	5·2
Breaking load (oz.)	18·9	23·3
Extension at break (%)	29	29

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P. P. TOWNEND

To the Editor, *Journal of the Textile Institute.*

MODES OF SWELLING AND SOLUTION OF FIBROUS NITROCELLULOSE OF HIGH NITROGEN CONTENT

As part of a study of nitrocellulose-solvent interaction, microscopic examination has been made of the action of a number of pure liquids and binary liquid mixtures on fibrous nitrocelluloses of high nitrogen content. It has been possible to distinguish certain modes of swelling and solution. The properties of the nitrocelluloses are given in Table I

The liquids used can be rather arbitrarily divided into:—

Solvents Acetone, cyclohexanone; methyl, ethyl and n butyl acetates; dimethyl, diethyl and dibutyl phthalates; diethyl and dibutyl tartrates; ethyl benzoate; diethyl succinate, triethyl citrate, triacetin, nitrobenzene; methyl alcohol (12·2 per cent. nitrogen only).

Non-solvents. Ethyl and n. propyl alcohols; ethyl ether; dioxane; benzene; hexane.

Table I

Nitrogen content, %	Origin	Viscosity of 0·2% solution in butyl acetate (Centipoises)
12·2	wood	1·38
12·55	cotton linters.	1·343
13·2	cotton waste	2·029

It should be noted that this division applies only to the range of nitrogen content covered and to single liquids. Ethyl alcohol and dioxane may dissolve lower nitrogen content material.[1] The solvent effect of alcohol-ether and alcohol-benzene mixtures is well known.[2] In addition to using pure liquids the action of binary mixtures containing 25 per cent and 50 per cent by volume of solvents with alcohol, benzene and hexane, where miscibility permitted, was also studied The action of acetone-water mixtures was also examined. Examination was carried out in both normal transmitted light and between crossed nicols, approximately 2 c.c. of liquid being added to a small quantity of fibres at room temperature and the effect noted, during and after addition.

Two modes of action of the solvents were distinguished.

(*a*) A process which may be termed "immediate gelation". The fibres immediately changed to structureless masses. The polarisation colour disappeared. With excess solvent and agitation the masses dispersed. This process was observed with acetone and alkyl acetates and all three nitrocelluloses.

(*b*) A slower process involving breaking of fibres into elongated fragments, followed by breaking of the fragments and eventual dispersion. This mode of solution obtained with all solvents other than those causing immediate gelation. This process, with ketones, has been observed by Mangenot and Raison.[3] The period required for complete disappearance of fragments varied from a few seconds with cyclohexanone to an hour or more with dibutyl phthalate. It appeared to be greater the more viscous the solvent and the higher the nitrogen content of the fibres. The polarisation colour persisted in the fragments.

With binary mixtures, low solvent concentrations resulted in almost immediate limited radial swelling, the polarisation colour becoming fainter. Increasing solvent concentration led to one of two modes of swelling. With mixtures involving acetone and all non-solvents, cyclohexanone with benzene and hexane, methyl and ethyl acetates with hexane, and diethyl phthalate with hexane, increasing solvent concentration led to axial contraction, together with further radial swelling. The polarisation colour disappeared. Further increase in solvent concentration gave rise to approximately spherical masses and finally to either immediate gelation or breaking into fragments. With other solvent—non-solvent mixtures increasing solvent concentration gave rise to further limited radial swelling with decreasing intensity of polarisation colour and finally to immediate gelation or breaking. Results obtained suggest that both degree and mode of swelling and the proportion of solvent just causing solution depend on at least three factors:

(*a*) The solvent used with a given non-solvent. Thus in alkyl acetate-benzene mixtures containing 25 per cent. solvent, ethyl acetate caused greater swelling than methyl or n. butyl acetate.

(*b*) The fibres used. Swelling often appeared to be greater the lower the nitrogen content, and there appeared to be smaller tendency for the 13·2 per cent nitrogen to pass into the axially contracted state. These variations, however, may reflect differences in structure rather than nitrogen content.

(*c*) The non-solvent used with a given solvent The proportion of acetone needed to cause solution was 90 per cent. in acetone-water, 70 per cent. in acetone-hexane, 50 per cent in acetone-alcohol and 20 per cent. in acetone benzene mixtures Swelling was generally least, for a given proportion of solvent, and the proportion of solvent required for solution greatest, when hexane was used as non-solvent Non-solvents alone caused limited radial swelling in some cases Dioxane swelled all three nitrocelluloses. Methyl alcohol swelled 13 2 per cent and 12·55 per cent. Ethyl alcohol swelled 12·2 per cent, but had little effect on the others

The types of solution process observed may possibly be interpreted in terms of fibre structure and molecular size of solvent. The solvents with the smallest molecules probably enter crystalline and amorphous regions[4] and cause immediate breakdown of structure Solvents with larger molecules may enter only amorphous regions or relatively open spaces in them [5] Breakdown of cohesion may occur at certain points resulting in breaking into fragments Further action of solvent may lead to a dispersion of crystalline regions [4] The two types of swelling may be tentatively interpreted in terms of solvent properties and fibre structure. The type involving axial contraction occurs in mercerisation and Valko[6] suggests that swelling permits extended chains to attain a more probable coiled configuration, causing shortening of fibres This may apply in the present case. The solvents involved in axial contraction are those which, from semi-quantitative swelling, viscosity and precipitation results,[7] can be regarded as poor solvents. With such solvents chains would be more likely to adopt a more contracted state. With better solvents, even of the same chemical type, extended chains will be favoured and only radial swelling observed.

The writer is indebted to Dr R. L Elliott and Mr. G. E. Styan for discussions during the course of this work.

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REFERENCES

[1] Kraus. *Nitrocellulose*, 1941, April, p. 63.
[2] Mardles. *Colloid Chem.* (Alexander), 4, 94.
[3] Mangenot and Raison. *Mem Serv. Chim de L'Etat*, 1944, 31, 276.
[4] Mathieu and Petitpas. *Trans. Faraday Soc.*, 1946, 42B, 17.
[5] Frey Wyssling. *Koll Zeit*, 1938, 85, 148.
[6] Valko "Cellulose and its derivatives" (Ott), p. 321.
[7] Moore. *Trans. Faraday Soc*, 1947, 43, 543.

The Editor, *Journal of the Textile Institute.*

Some Observations on the Influence of Fabric Structure on Felting

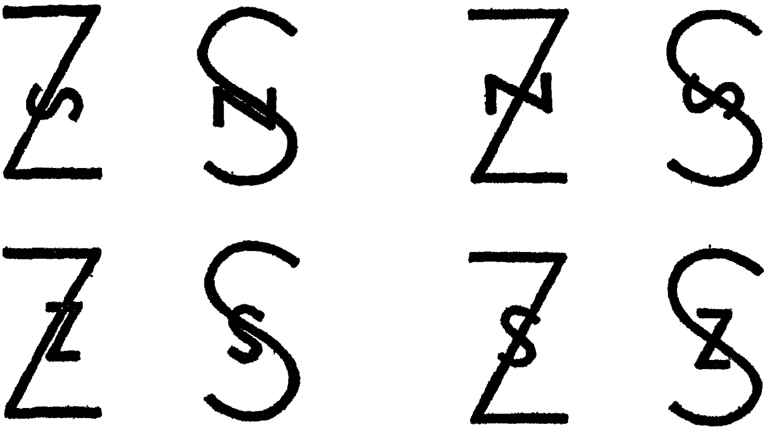
Felting, as is well known, is a function of the mobility of the fibres and yarns in a fabric. It is also known that certain structural features, such as the relationship between the direction of twist of the warp and weft yarns,[1] affect the compactness of a fabric and hence the freedom of movement of the yarns and of the fibres.

We have observed that the susceptibility to felting is also affected by the relationship between the direction of the twill line in twill or satin fabrics and the direction of twist of the warp and weft yarns.

If we use the letters S and Z to indicate the direction of twist in the accepted manner (S: clockwise, Z: anticlockwise) and also to indicate the direction of the line of twill (S: down to the right, Z: down to the left) the following relationship has been found to exist between the twist of yarn and the line of twill in respect of susceptibility to felting.

Twist of Yarn.	*"S" Twill.*	*"Z" Twill.*
Warp S	Low	High
Z	High	Low
Weft S	High	Low
Z	Low	High

It can be seen from this table that the susceptibility to felting is greater when the twill and twist directions cross than when they do not. If large letters are used for the direction of twill and small letters (vertical for warp: horizontal for weft) for the yarn twist, the relationship can be represented pictorially:—



These constructions also appear to have a considerable influence on the properties of fabrics made from spun rayon and from cotton. It is known that in spun rayon fabrics, when roughened up by the friction of vigorous washing, the fibres can mat together to give rise to a phenomenon similar to the felting of wool. We have found that this also is governed by the above relationship of twill and twist. A similar effect has been observed with certain cotton fabrics

These observations have been made on laundered wool, rayon and cotton articles and the phenomenon is being further investigated

The authors wish to express their thanks to the Director of Research for permission to publish this note.

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REFERENCE

[1] Strong, J. H *Foundations of Fabric Structure.* p 21.

CORRECTION

Effects of Strain on the Microscopic Structure of Acetate Rayon—Simmens and Howlett.

Page 597—The first four lines at the top of this page should follow the third line in the paragraph commencing "The results of these investigations, etc. . . "

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TRANSACTIONS

45—AN ENUMERATION PROBLEM IN TEXTILE DESIGN
PART II.

By S. A. SHORTER

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I. INTRODUCTION AND SUMMARY
II THE GROUP OF OPERATIONS
III THE GROUP SYMMETRIES

I. INTRODUCTION AND SUMMARY

Part I of this work* dealt with certain fundamental conceptions indispensable to an adequate theory of the "cycle of steps", this having been exemplified in its simplest form as an "elementary design", that is a design in which, on any one pick, only a single warp thread is raised within the weftway repeat, and any particular warp thread is raised only once within the warpway repeat. The theory developed was applied to the solution of the problem of "enumerating" the elementary design, using the term to denote, in its present connexion, the finding and application of formulæ for the calculation of the number of designs of any period. The problem of "enumerating" the elementary designs in the other sense of the term, that is, of specifying them *seriatim*, will be considered in Part III of this work

The elementary design was defined so as to make its individuality depend not merely on a certain intrinsic arrangement of design points, but also on the relation of this to an external frame of reference. This led to the definition of a new entity, the "primitive pattern", to denote the arrangement of points considered apart from the frame of reference The present paper deals with the relation between the elementary design and primitive pattern, a subject relevant to a number of problems, in particular to the problem, previously mentioned, of specifying the designs *seriatim*, or what may conveniently be called the problem of "detailed" enumeration

In Section II of the present paper a study is made of the operations which change the relation of a design to the external frame of reference, and which in general yield a different design. It is shown that these operations, with the "identity" operation, form a mathematical "group" of well-known type The designs obtained from any given design by the operations of the group are called its "group-derivatives". Together with the original design they constitute the complete set of designs corresponding to a single primitive pattern. In pursuance of the plan, adopted in Part I, of replacing the customary graphical by numerical procedures and modes of specification, it is shown that the geometrical operations of the group correspond to certain simple numerical operations performed upon arrays of steps and co-ordinates.

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* In part I a convention was adopted, which, though a recognised one, would appear to require some explanation in its application to the specification of sub-periodic designs This is the use of an index notation to indicate the repetition of a symbol or group of symbols. According to this, for example, the array 22222 is written 2^5, and the array 255255255 is written $(255)^3$, and the general form for the array of steps of a sub-periodic design of period *m* (=*an*) and order *n* was taken in Part I as $(s_1 s_2 \ldots s_a)^n$

Ordinarily, the group-derivatives of a design are different from the design, and form with it a set of eight designs corresponding to the same primitive pattern; but there are certain designs which are unaffected by one or more operations of the group, this invariance denoting the possession of certain types of symmetry. These are investigated in Section III, where the algebra of the group is developed so as to determine the types of symmetry which are possible. It is shown that there are nine types (or ten, if designs with none of the symmetries of the group are regarded as constituting a type); and that these include five "lowest" types, for which the number of designs corresponding to the same primitive pattern is reduced to four, three "higher" types, for which the number is reduced to two, and a single "highest" type, for which a primitive pattern corresponds to only one design. The numerical procedure for obtaining the group-derivatives of a design, devised in Section II, is illustrated for designs exemplifying all the nine types of symmetry. In this application, the procedure constitutes a routine for determining the symmetry of designs, and their mode of association, to correspond to the same primitive pattern, a routine, moreover, by means of which the results of a detailed enumeration of designs may be abbreviated to an enumeration of primitive patterns.

This theory of symmetry differs in many respects from a more general theory applicable to all classes of designs repeating in two directions over a plane—a theory developed some twenty-four years ago as an offshoot from that of crystal symmetry. To conclude Section III the relation between the two theories is briefly considered.

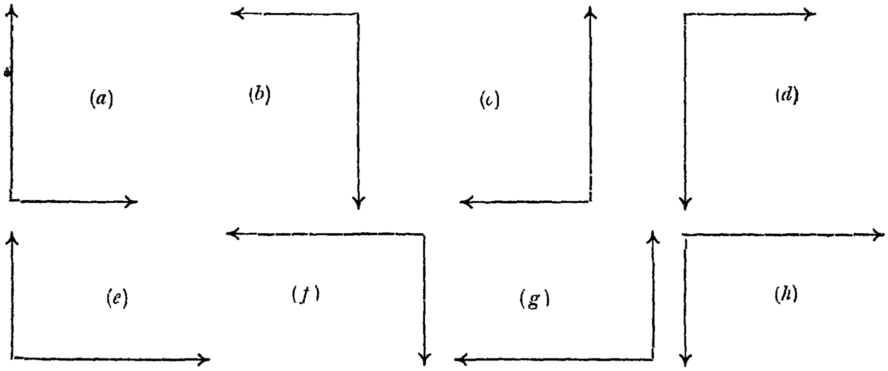
II. THE GROUP OF OPERATIONS

A graph intended to be the R.P.A of an elementary design does not actually become one until directions "rightward" and "upward" have been assigned along the lattice lines in one of the eight possible ways. To have complete freedom in this assignment, one must imagine the graph to be drawn on a sheet of transparent material, so that it may be viewed from either side. Previous to the assignment the graph may be regarded as representing a primitive pattern. The assignment determines the relation of the graph to an external frame of reference. According to a literal interpretation of the term "upward", the frame of reference must be visualised as a vertical wall to which the sheet of material must be fixed, so that the indicated directions are correct. In practice, of course, the term is used according to the convention whereby one speaks of the "top" of a page or sheet of paper, which need not be vertical, and may even be horizontal, the "upward" (and "rightward") being determined by the position of the observer.

After this assignment, the cycle of steps may be made determinate by adopting a standard method of stepping. This was done in Part I, the standard method being stepping upwards while traversing the columns of the design from left to right. This is one of eight possible methods, which include, for example, stepping to the left while traversing the rows of the lattice downwards.

After the graph has been placed in any assigned relation to the frame of reference, so as to produce a definite design, this relation may be changed to seven others by means of suitable "operations". The nature of these operations may be deduced from a consideration of the figure. The two arms of the L-shaped "indicator" represent the assigned directions marked on the graph, the short arm of the L the "rightward" direction, and the long arm the "upward". At (*a*) these lie in the correct assigned directions, corresponding to the original design. At (*b*) both directions have been reversed; at (*c*) only the horizontal; at (*d*) only the vertical These exhaust the possibilities when the horizontal arm remains horizontal, and the vertical, vertical; or in other words, when there has been no interchange of warp and weft directions. At (*e*) there has been such an interchange, the arms, however, still pointing the one rightward and the other upward At (*f*) both these new directions have been reversed, at (*g*) only the horizontal, at (*h*) only the vertical.

It will be seen that the design corresponding to (*b*) is the result of turning the one corresponding to (*a*), that is, the original design, upside down: and that the designs corresponding to (*g*) and (*h*) are the results of rotating the original design through a right angle in its plane, respectively anti-clockwise and clockwise. To produce the designs corresponding to (*c*), (*d*), (*e*) and (*f*) by the imaginary process of fixing the sheet of material to the vertical wall, it would be necessary to turn it "back to front" before fixing it with the four requisite orientations These could be obtained from the sheet placed so as to give the original design by rotating it through two right angles about lines in its plane, these lines running, for (*c*) vertically, for (*d*) horizontally, for (*e*) upwards to the right in the direction making equal angles with the horizontal and vertical, and for (*f*) upwards to the left similarly. It is more convenient, however, to imagine these changes to be the results of reflecting the design in a mirror placed with its plane normal to that of the design and intersecting it in lines having these four respective directions. Adopting a usual convention, one may refer to these reflections as reflections in the lines themselves.



If leaving the design unaltered is regarded as an operation (analogous to the operation of multiplication by unity in ordinary algebra) there are eight operations which form a mathematical "group" of well-known type, involving reflections and rotations The operations have the property, characteristic of these of a group, that the result of performing two operations in succession is the same as that of one of the single operations Thus reflecting in a horizontal line and then turning upside down produces the same result as reflecting in a vertical line. Moreover, corresponding to each operation there is an inverse operation annulling its effect. Thus an anti-clockwise right angle rotation is the inverse of a clockwise right angle rotation. Actually all the other operations of the group are self-inverse, performed twice in succession they yield the original design.

The eight operations of the group are exhibited in Table I, each with a symbol or "operator" denoting it.

Table I
The Group of Operations transforming the Elementary Design

Description of Operation	Operator
Leaving the design unaltered—the "identity" operation .. .	E
Turning it upside down	U
Reflecting it in a vertical line	V
Reflecting it in a horizontal line	H
Rotating it clockwise through a right angle	C
Rotating it anti-clockwise through a right angle	A
Reflecting it in a line running upwards to the right making half a right angle with the horizontal and vertical	R
Reflecting it in a line running similarly upwards to the left	L

With appropriate conventions these operators may be manipulated somewhat after the manner of ordinary algebraical symbols. A number of operators written in the form of an algebraical product will be taken to denote the compound operation of performing the indicated operations in order from right to left. Thus VU denotes the compound operation of turning a design upside down and then reflecting it in a vertical line, CVU the compound operation of, in addition, subsequently rotating the design clockwise through a right angle. An index notation is used to denote the repetition of an operation: thus V^2 is equivalent to VV, C^3 to CCC and so on. Any compound operation is equivalent to a single operation. Thus VU is equivalent to H, LVU to C. Such equivalence will be indicated by the sign of equality. Thus VU=H and LVU=C.

Excluding the identity operator, there are 49 two-term "products", and these may be evaluated by operating on the symbols formed by the indicator in the figure, starting with (*a*) which corresponds to the original design. The symbols (*b*), (*c*), (*d*), (*e*), (*f*), (*g*) and (*h*) are, of course, the respective results of the operations U, V, H, R, L, A and C, and performing these seven operations on the seven symbols determines these products. For example, reflecting (*g*) in a horizontal line yields (*f*) so that HA=L.

Table II
Multiplication Table of the Group of Operations transforming the Elementary Design

	E	U	V	H	R	L	A	C
E ..	E	U	V	H	R	L	A	C
U .	U	E	H	V	L	R	C	A
V ..	V	H	E	U	A	C	R	L
H ..	H	V	U	E	C	A	L	R
R .	R	L	C	A	E	U	H	V
L	L	R	A	C	U	E	V	H
A .	A	C	L	R	V	H	U	E
C .	C	A	R	L	H	V	E	U

The complete "Multiplication Table" of the group is shown in Table II. In this, any operation in the body of the Table is the equivalent of the operation at the head of the occupied column, followed by the one at the end of the occupied row. Thus AV=L, RV=C and so on. The Table includes rows and columns designated by the identity operator, these being analogous to the "one times" and "so many times one" entries of the ordinary multiplication table.

This algebra may be extended to include symbols indicating the entities operated upon. These will be denoted by heavy type capital letters Thus if **D** denote a certain design, **HD** will denote the design obtained by reflecting it in a horizontal line. Such designs will be termed the *group-derivatives* of the original design, the operation involved being prefixed to the symbol denoting the design Thus **HD** will be called the H group-derivative. Compound operators may be applied to the symbol denoting the design, forming compound group-derivatives, but these are readily converted to simple group-derivatives by the help of the multiplication table. Thus LVR**D**=V**D**.

An equation of this kind is analogous to an ordinary algebraic identity involving, say, a variable x, in that it is true for any type of design, just as the algebraic identity is true for any value of x. On the other hand, one can form equations, analogous to conditional equations in ordinary algebra, which are true only for certain types of design. An example of such an equation is V**D**=H**D**. From this kind of equation one can deduce others by multiplying each side by the same operator. Thus in the case of this particular example, multiplying both sides by R gives the equation RV**D**=RH**D**, which reduces to C**D**=A**D**, showing that if a design is such that the results of reflecting in a vertical and a horizontal mirror are the same, so are the results of a clockwise and an anti-clockwise right angle rotation

The eight operations of the group have a one-to-one correspondence with the eight possible methods of stepping, based on the fact that each operation converts a non-standard method into the standard method, except in the case of the identity operation, where the standard method remains standard. This correspondence is exhibited in Table III.

Table III
The Correspondence between the Operations of the Group and the possible Methods of Stepping

Operation	Methods of Stepping in original Design which become standard in the transformed Designs	
	Step	Traverse
E	upwards	to the right
U	downwards	to the left
V	upwards	to the left
H	downwards	to the right
C	to the left	upwards
A	to the right	downwards
L	to the left	downwards
R	to the right	upwards

It will be convenient to refer to these methods as stepping "upwards to the right", "downwards to the left", and so on, the first direction mentioned relating to the step, and the second to the traverse The cycle of steps of any group-derivative may be obtained from the original design by the appropriate non-standard method of stepping. Thus for the C group-derivative one would step "to the left upwards" on the original design

By a consideration of these non-standard methods, and the group-derivatives to which they correspond, it is possible to devise purely numerical procedures by means of which one can deduce the array of steps of any group-derivative from that of the original design Let P and P^1 be two adjacent design points in the same column of the original design, P^1 being above P; and let Q be the design point above P and below P^1 in the next column to the right. The standard method of stepping, when the line between the two columns is crossed, will yield the step from P to Q The method of stepping "downward to the left" will yield the step from Q to P, a step of the same magnitude, but in such a direction that the order of successive steps is reversed. Hence the cycle of steps of the U group-derivative is the reverse of that of the original design.

The method of stepping "downwards to the right" will yield the step from $P^1$to Q, this being complementary to that from P to Q, in the sense that the sum of the two steps is equal to the period Successive steps will be taken in the original order Hence the cycle of steps of the H group-derivative will consist of the complements of the steps of the original cycle taken in the same order Stepping "upwards to the left" reverses this order, so that the cycle of steps of the V group-derivative will consist of the complements of the steps of the original design, taken in reverse order

The R, L. A and C group-derivatives involve interchange of the warp and weft directions. The design corresponding to (*e*) in the figure is the R group-derivative of the original design, and in (*e*) the rightward and upward directions have been preserved, though the directions of the long and short arms have been interchanged. It follows from this that a co-ordinate array of the R group-derivative may be derived from a co-ordinate array of the original design by the process of interchanging the explicitly stated "*y*" co-ordinates with the implied "*x*" co-ordinates The new array may be written down directly from an inspection of the old array, by examining, in the latter, each term in order of magnitude, and writing down in succession each implied co-ordinate, as deduced from the position of the examined term Thus, if the old array of co-ordinates were 2 4 3 5 1, the process would be as follows·

1 occurs in the 5th place, so write down 5
2 „ „ „ 1st „ „ „ „ 1
3 „ „ „ 3rd „ „ „ „ 3
4 „ „ „ 2nd „ „ „ „ 2
5 „ „ „ 4th „ „ „ „ 4

so that the new array is 5 1 3 2 4 In general the problem will be to obtain an array of steps of the R group-derivative, given that of the original design It will then be necessary to deduce an array of co-ordinates from the original array of steps, and after the interchange of co-ordinates, convert the new array of co-ordinates into an array of steps

The procedure for deducing a complete set of group-derivatives is illustrated below for the design 5 1 4 2 3 4 6 7. The U, V and H group-derivatives have been obtained by the respective operations of reversing the original array of steps, converting the terms of this new array to complements, and reversing this complementary array After this, an array of co-ordinates* was deduced from the original array of steps, taking 1 as the first co-ordinate The process of interchange of co-ordinates was then carried out, and the new array of co-ordinates converted to an array of steps Operations on this array, similar to those performed on the original array, then yielded the arrays of steps of the remaining group-derivatives.

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*The use of arrays of co-ordinates and arrays of steps in the same immediate context need not cause any confusion, as the two types of array are readily distinguished by the fact that an array of co-ordinates contains a term equal to the period (e g. 51324) while an array of steps does not (e.g 12421)

D	5	1	4	2	3	4	6	7	
UD	7	6	4	3	2	4	1	5	
VD	1	2	4	5	6	4	7	3	
HD	3	7	4	6	5	4	2	1	
D	1	6	7	3	5	8	4	2	
RD	1	8	4	7	5	2	3	6	
RD	7	4	3	6	5	1	3	3	
LD	3	3	1	5	6	3	4	7	(=URD)
AD	5	5	7	3	2	5	4	1	(=VRD)
CD	1	4	5	2	3	7	5	5	(=HRD)

The particular example chosen is one for which all the group-derivatives are different. Certain designs, however, are invariant to one or more of the operations of the group This invariance denotes the possession of certain types of symmetry, and these are investigated in the following Section

III. THE GROUP SYMMETRIES

If a design is unaffected by being turned upside down, that is to say, if it is invariant to the operation U, it will be said to be U symmetrical; and a similar notation will be used for the other operations of the group. If a design is unaffected by a clockwise right angle rotation, it will also be unaffected by an anti-clockwise right angle rotation, and *vice versa,* for the effect of the one operation is the same as that of the other repeated three times in succession Hence C symmetry and A symmetry are the same property, and henceforth only the former term will be used Two right angle clockwise rotations turn the design upside down Hence all C symmetrical designs are also U symmetrical but the converse of this is not true.

The identity of two group-derivatives always implies a certain type of symmetry. Thus if VD=HD, multiplication of both sides of the equation by V gives $V^2D=VHD$, which reduces to D=UD, indicating that the design is U symmetrical There are 21 equations expressing the identity of two group-derivatives, and these can be derived from the equations expressing the identity of a group-derivative with the original design by multiplying each of these latter by the operators in the order given in Tables I or II, omitting the process for operators involved in previous equations For each of the types of symmetry, U, V, H, R and L, there is thus a set of four equations, while for C symmetry there are two such sets, since there are two equations expressing the identity of the original design and a group-derivative The 28 equations are exhibited in Table IV, classified under the headings of the types of symmetry they indicate in the original design

Table IV
Equivalent Symmetry Relationships

U symmetry	V symmetry	H symmetry	R symmetry	L symmetry	C symmetry	
D=UD	D=VD	D=HD	D=RD	D=LD	D=CD	D=AD
VD=HD	UD=HD	UD=VD	UD=LD	UD=RD	UD=AD	UD=CD
RD=LD	RD=CD	RD=AD	VD=AD	VD=CD	VD=LD	VD=RD
AD=CD	LD=AD	LD=CD	HD=CD	HD=AD	HD=RD	HD=LD

By means of these relationships, it is possible to deduce the consequences of the co-existence of any two types of symmetry. Not counting the co-existence of U and C symmetries, which is an inevitable result of the existence of the latter type, there are 14 possible combinations of two types. Considering first the co-existence of U and V symmetries, it will be seen from the first column of Table IV that **D = UD**, from the second column that **UD = HD**, from the first again that **HD = VD**, and finally from the second, that **VD = D**. Hence the original design and its U, V and H group-derivatives must be all identical. The same result follows from assuming the co-existence of either U and H, or V and H symmetries There is therefore a type of symmetry characterized by the identity of the U V and H group-derivatives with the original design This will be termed UVH symmetry It may readily be shown that this type is further characterized by the identity with each other of the R, L, A and C group-derivatives

In a similar manner it may be shown that there is a type, which will be termed URL symmetry, characterized by the identity of the U, R and L group-derivatives with the original design, and further by the identity with each other of the V, H, C and A group-derivatives, this type being deducible from the co-existence of any two of the types U, R and L.

From the equations in the sixth and seventh columns of Table IV it may be shown that C symmetry is characterized by the identity of the U, C and A group-derivatives with the original design, and further by the identity with each other of the V, H, L and R group-derivatives

The relationships for C, UVH and URL symmetries are exhibited in Table V.

Table V
Relationships characteristic of C, UVH and URL symmetries

C symmetry	UVH symmetry	URL symmetry
D = UD = CD = AD VD = HD = LD = RD	D = UD = VD = HD RD = LD = AD = CD	D = UD = RD = LD VD = HD = CD = AD

The above discussion deals with six of the fourteen pairs of types The co-existence of any of the remaining eight pairs involves the identity of all the group-derivatives with the original design In the case of any of the four pairs V or H with R or L, one may pass to and fro between the relevant columns of Table IV, so as to form a closed chain of equations establishing this identity Thus, assuming the co-existence of V and R symmetries one obtains the closed chain **D = VD = AD = LD = UD = HD = CD = RD = D.** In the case of any of the four pairs, C with V, H, R or L, the same result follows from the linking together of the two sets of equations in the first column of Table V. This type of symmetry, in which a primitive pattern yields the same design in whichever of the eight relations to the frame of reference it is placed, will be termed "complete group" symmetry, abbreviated to CG symmetry

There are thus nine types of symmetry, five "lowest" types (U, V, H, R and L), three "higher" types (C, UVH and URL) and one "highest" type (CG) A design conforming to the requirements of a lower type may happen to conform to those of one or more higher types If it is desired to exclude these latter types, the symmetry symbol will be enclosed in square brackets For example a design which is invariant to being turned upside down is U symmetrical, and if it is invariant to no other operation of the group it will also be termed [U] symmetrical. The complete set of U symmetrical designs will include all those which have the symmetries [U], [C], [UVH], [URL] and CG. The complete set of V symmetrical designs will similarly include all those which have the symmetries [V], [UVH] and CG and so on For the "higher" types C, UVH and URL, the brackets will denote simply the exclusion of CG symmetry.

The symmetries denoted by unbracketed symbols are of importance in relation to routines of enumeration devised for particular types of symmetry, since, in general, such routines yield designs with the relevant higher types On the other hand, the symmetries denoted by bracketed symbols are of importance in the more immediate problem of the relation between designs and primitive patterns.

A design with none of the symmetries of the group is one of a set of eight designs corresponding to the same primitive pattern. Given an array of steps of any one of these eight, arrays of steps of the other seven may be deduced by means of the procedure described at the end of the preceding Section For any period the complete series of such designs is represented by one-eighth their number of primitive patterns

The equations shown in Tables IV and V indicate the relationship between designs and primitive patterns for the different types of symmetry A [U] symmetrical design is not V, R or L symmetrical It follows, therefore, from the four equations in the first column of Table IV, that such a design is one of a set of four, corresponding to the same primitive pattern, the others being its V (or H), its R (or L) and its A (or C) group-derivatives. All the designs will be U symmetrical, and for any period the complete series of U symmetrical designs is represented by a quarter their number of primitive patterns

A [V] symmetrical design is not U, R or L symmetrical It follows therefore from the four equations in the second column of Table IV that such a design is one of a set of four corresponding to the same primitive pattern, the others being its U (or H), its R (or C) and its L (or A) group-derivatives The first of these three will be [V] symmetrical, like the original design, but the two others will be H symmetrical, owing to the interchange of warp and weft directions. For any period the complete set of [V] symmetrical designs consists of pairs of mutual U group-derivatives, and from this set there can be deduced the complete set of [H] symmetrical designs by means of the operation R or L, (there being a one-to-one correspondence between the two sets based on either of the two operations). The number of primitive patterns corresponding to both sets of designs is thus equal to a quarter the total number, or half the number in either set

Similar considerations apply to designs with [R] and [L] symmetry, the four designs corresponding to the same primitive pattern being related as indicated in the fourth (or fifth) column of Table IV

A [C] symmetrical design is not V symmetrical, a [UVH] symmetrical design is not R symmetrical, a [URL] symmetrical design is not V symmetrical, so that for each of these types of symmetry, a design is one of a pair, related as indicated in the relevant column of Table V, corresponding to the same primitive pattern, the number of these primitive patterns, for any period, being half the number of corresponding designs

The procedure for obtaining the group-derivatives of a design, described in the previous Section, when applied to a design having one of the symmetries of the group, replicates it in a manner which reveals the type of symmetry, and yields the designs, four, two or only one in number, which correspond to a single primitive pattern This is illustrated in Table VI for designs which exemplify all the nine types of symmetry In this, each

Table VI. The Group-derivatives of Symmetrical Designs

	I	II	III	IV	V	VI	VII	VIII	IX
D	122322	23642564	122544	1326414	11112163	265262562	23246564	125352	223443
UD	223221	46524632	445221	4146231	36121111	265262562	46564232	253521	344322
VD	443445	42364256	221445	3631546	52767777	734737437	42324656	413145	322344
HD	544344	65246324	544122	6451363	77776725	734737437	65642324	541314	443223
D	124635	13648275	124653	1257634	12345786	139574628	13684275	124365	135264
RD	125364	16248375	126354	1267354	12345867	182647593	16258374	124365	142635
RD	134343	54243464	143253	1413264	11113612	734737437	54333455	125352	344322
LD	343431	46434245	352341	4623141	21631111	734737437	55433345	253521	223443
AD	323235	42454643	314325	3154636	67257777	265262562	33455543	413145	443223
CD	532323	34645424	523413	6364513	77775276	265262562	34555433	541314	322344
	[U]	[V]	[H]	[R]	[L]	[C]	[UVH]	[URL]	CG

Table VII

Illustrating the less usual modes of exemplification by the Elementary Design of the symmetry types of the General Theory

A	[R]	W3	Set of symmetry axes in one direction	$(2, 11, 4, 11, 11, 3)^2$
B	[R]	W4	Set of screw axes in one direction	$(13, 2, 15, 4, 2, 15, 14, 7)^2$
C	[URL]	W5	Sets of symmetry axes in two mutually perpendicular directions	$(2721)^2$
D	[URL]	W6	Set of symmetry axes and set of screw axes in mutually perpendicular directions	$(10, 1, 3, 1, 10, 5)^2$
E	[URL]	W7	Sets of screw axes in two mutually perpendicular directions	$(2, 7, 2, 9, 10, 7, 10, 9)^2$

column of eight arrays of steps and two auxiliary arrays of co-ordinates, has at its head a reference numeral for the design, and at its foot an indication of the symmetry

It will be seen, for example, that with design I, the original array of steps and that of the U derivative represent the same design, so that the design is U symmetrical, while all the other arrays of steps represent designs differing from the original, so that the design is [U] symmetrical Moreover the eight arrays represent four different designs, which are duplicated in accordance with the equations in the first column of Table IV Similar considerations apply to designs II, III, IV and V, where the designs are duplicated, and to designs VI, VII and VIII, where they are quadruplicated For design IX the identity of all the designs represented indicates "complete group" symmetry

Considerations of symmetry enable the results of a detailed enumeration to be abbreviated to a list of primitive patterns by selecting one design from each of the sets of designs corresponding to the same primitive pattern, at the same time specifying the symmetry of the selected design. The selection of the design, thus representing the primitive pattern, could be made arbitrarily. but when the problem of detailed enumeration is considered in Part III of this work, a definite criterion will be adopted to govern this selection, one arising, moreover, naturally out of the routine of enumeration The complete list of designs would be implicit in the list of primitive patterns, and could be recovered by operating on the specified arrays in accordance with the symmetry indications. Thus an array representing a design stated to have none of the symmetries of the group, would have to be supplemented by seven other arrays· an array representing a design stated to have [U] symmetry would have to be supplemented by three others obtained by the numerical procedures corresponding to the operations V, R and A: and so on, the "higher" types [C], [UVH] and [URL] involving one extra array and CG symmetry none

There are two general characteristics of a design which limit its possible types of symmetry. In the first place, no design of odd period can be V or H symmetrical, so that the only possible bracketed types for such designs are [U], [R], [L], [C] and [URL] Secondly, the same limitation applies to sub-periodic designs, if one excepts the single design 1^2 ("plain weave").

It can readily be shown that designs with V or H symmetry must have an even period This follows from the fact that, with such designs, the set of steps in the cycle is identical with the set of complementary steps. Making use of equation (1) of Part I, one can write $\Sigma s = \Sigma(m-s) = Mm$, where Σ denotes summation of the steps s over the complete cycle From these equations it follows that $\Sigma s = \frac{1}{2}m^2$ and $M = \frac{1}{2}m$. Since M is integral m must be even.

Equation (2) of Part I, relating to the cycle of steps of a sub-periodic design, may be written in the form $n\Sigma s = Mm$, where Σ now denotes summation over the sub-cycle of steps. As pointed out in Part I, n and M must not contain a common factor, as otherwise, by division, the above equation could be made to yield an equation denoting that a partial sum of consecutive terms was divisible by the period. Such divisibility is impossible if $M=1$, in which case the design is the simple twill 1^m For such a design to be V or H symmetrical the period, as has just been shown, must be equal to $2M$, in this instance to 2. Hence the only twill with either of these types of symmetry is the design 1^2.

If $M>1$, the condition necessary for V or H symmetry is that n and $\frac{1}{2}an$ ($=M$) should be mutually prime. This is impossible, for since $\frac{1}{2}an$ is integral, one at least of the two numbers a and n must be even, and therefore $\frac{1}{2}an$ must have as a factor either n or $\frac{1}{2}n$

To conclude this investigation of the symmetries of the elementary design, it seems desirable to relate it to a more general theory of the symmetry of designs which originated as a development of the theory of crystal symmetry This theory is applicable to all types of design which repeat in two directions over a plane, to textile designs in general, and to designs not based on a warp and weft structure, such as could be used, for example, for a printed fabric or wallpaper The types of symmetry possible in such designs have been enumerated by Polya,[2] and further considered by Niggli[3] in a crystallographic journal These authors have treated the subject from the point of view of general crystallographic theory, applying to a space of two dimensions conceptions originating from a consideration of a space of three dimensions, but a more direct approach to the subject, one more relevant to textile design, has been given in a paper by H. J. Woods[1] in this *Journal* In the following discussion the brief descriptions of these types according to the general theory will be supplemented by references (W1, W2, *etc.*) to Table I and Fig. 1 of that paper, where the types are described in more detail and illustrated by diagrams

According to the general theory there are six fundamental types of symmetry, axial symmetry, screw symmetry and four types of central symmetry, twofold, threefold, fourfold and sixfold, these latter being invariance to rotations, respectively, a half, a third, a quarter and a sixth of a complete revolution There are in addition a number of compound types Since in the special theory of the present Section the operations contemplated are restricted to those which maintain the horizontal and vertical directions of the lattice lines, there are no types corresponding to threefold and sixfold central symmetries; and [U] and [C] symmetries correspond respectively to simple twofold and fourfold central symmetries (W2 and W10).

Axial and screw symmetries give rise, in different ways, to the identity of a design and its reflection On an axially symmetrical design it is possible to locate the reflecting line so that there is exact coincidence between the various features of the reflection and those of the overlaid portions of the original design, the reflecting line then lying along a "symmetry axis". With a screw symmetrical design, this is not possible, but the reflecting line may be located so that this coincidence is obtainable if the reflection is displaced in the direction of the line by an amount equal to half the distance on which the design repeats in that direction, the reflecting line then lying along a "screw axis". On an extended repeat of either type of design, these axes form a set of parallel lines, evenly spaced at half the distance on which the design repeats in the direction normal to them

The distinction between axial and screw symmetry is not directly relevant to the theory of the present Section, for with either type the reflection does not change the cycle of steps· and actually the mirror symmetries (V, H, R and L) exemplify among them both types Except in the solitary instance of the design of period 2, axial symmetry is impossible along warpway and weftway axes, and designs with [V] and [H] symmetry exemplify simple screw symmetry (W4), and those with [UVH] symmetry a compound type with screw axes in two mutually perpendicular directions (W7).

Axial symmetry is possible, however, in the two diagonal directions, and both this type and screw symmetry are exemplified by [R] and [L] symmetrical designs If they are non-sub-periodic they exemplify a compound type (W8) with alternating parallel screw and symmetry axes. If they are sub-periodic, they may exemplify any one of three types, simple axial symmetry (W3), simple screw symmetry (W4), or the above-mentioned compound type (W8), these possibilities being closely related to the character of the basis of enlargement. Designs with [URL] symmetry, if they are non-sub-periodic, exemplify a compound type (W9), in which parallel symmetry and screw axes alternate in both of two mutually perpendicular directions Sub-periodic [URL] symmetrical designs exemplify among them four types in the general theory, the above-mentioned compound type (W9), and the types characterized by symmetry axes in two mutually perpendicular directions (W5), by similar screw axes (W7), and by symmetry axes in the one direction and screw axes in the other (W6).

Designs with CG symmetry combine the criss-cross of warpway and weftway screw axes, characteristic of [UVH] symmetry, with a criss-cross of alternating diagonal symmetry and screw axes, characteristic of the [URL] symmetry of non-sub-periodic designs This exemplifies a type (W12), which is one of the two compound types in the general theory involving fourfold central symmetry The other type (W11) is exemplified only by the single design of period 2 ("plain weave"), in which there are symmetry axes in the two diagonal directions, and alternating symmetry and screw axes warpway and weftway

It is beyond the scope of the present paper to do much more than describe briefly, in the above manner, the relation between the types in the two theories. By plotting the designs of Table VI, it may readily be shown that they exemplify the types in the general theory as stated above. As illustrations of the less usual modes of exemplification, exhibited by certain varieties of sub-periodic designs, five designs are shown in Table VII In this, the symmetry of each design is specified according to both theories, a reference being given to the numbered types in the paper of H. J. Woods, and each design has been given a reference letter (A, B, *etc.*). It has not been considered necessary to include designs with [L] symmetry, since they may easily be derived from designs A and B by conversion of the arrays of steps to complementary arrays.

These five designs illustrate simple methods of synthesis of the various types. Design A is formed from a motif having axial symmetry about the rightward-upward diagonal of the cell in which it is contained, the motif being distributed on a "plain weave" basis. Design C is formed similarly from a motif symmetrical about both diagonals of its cell. (This double symmetry is a sufficient, but not necessary condition for the type W5, the design $(252)^2$ for example, being formed from a motif symmetrical about only one diagonal, and yet having this type of cymmetry) Designs B, D and E are based on a sub-division of the cell into quarter squares, and the means adopted for obtaining the various types of symmetry are fairly evident from graphs of the designs. The various synthetic processes may readily be made more general by adopting other suitable bases of enlargement, and spreading the design points over more than one set of cells

If designs with none of the symmetries of the group are regarded as constituting a type in the theory of the present Section (corresponding to the type W1 in the general theory), and if the design 1^2 is included as the sole exemplification of the type WII, it will be seen that the elementary design exemplifies all the types in the general theory, twelve in number, which do not involve threefold or sixfold central symmetry. There is, however, no "correspondence" in the mathematical sense, in either direction, between the two series of types, that is to say, there is not, for each type in one theory, a unique corresponding type in the other.

REFERENCES

[1] Shorter. *J Text. Institute*, 1949, **40** T189
[2] Polya. *Zeits fur Krist*, 1924, **60**, 278
[3] Niggli. *Ibid.*, 1924, **60**, 283
[4] H. J. Woods *J Text. Institute*, 1935, **26**. T341.

Didsbury, Manchester.

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46—THE POROUS PLUG AND FIBRE DIAMETER MEASUREMENT.

EFFECT OF FIBRE ORIENTATION AND USE OF PLUGS OF RANDOMIZED FIBRES

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1. INTRODUCTION AND SUMMARY

In a previous paper Cassie[1] discussed the use of plugs of parallel fibres for determination of fibre diameter by an air flow method. The fibre diameters of a range of wool tops were found from the projector and the shape factor *k* in the Kozeny equation was determined from air flow results. A further investigation has shown that the degree of fibre parallelism in tops may be sufficiently variable to make the use of parallel plugs inaccurate in particular cases for determination of diameter. If diameter is measured by some other method, the air flow results on parallel plugs throw light on the amount of fibre parallelism

For more accurate determination of fibre diameter a method of preparing packed beds of cut and randomized fibre pieces has been developed which gives results independent of the initial fibre arrangement.

A modification of the original equations is discussed, which allows for slip of the gas molecules at the pore boundaries

2. EXPERIMENTAL DETAILS

The apparatus which is shown in Fig. 1 is substantially the same as that described in the earlier paper but modified in the light of experience A is an inverted aspirator bottle fixed to a stand and connected by rubber tubing to the container B which is open at the top. The plug of fibres is formed in a short length of brass tube C pushed into the hole in the rubber cork and then into the mouth of A as shown The container B is then lowered to a stop near the base of the stand and the liquid (distilled water) begins to rise in B and draws air from the room through the plug. The time taken for the level to rise from the marks 0 to 3 on B is taken and the fibres are then pushed out of the tube and weighed. The time t_0 taken for the level to rise from 0 to 3 with no fibres present is also obtained and this correction is subtracted from the observed time.* Since air from the room is drawn through the plug the apparatus is used at constant temperature and relative humidity.

Measurements of fibre diameter were made with the projection microscope in the usual way The fibre pieces were previously conditioned at 65 per cent. R.H. before being dispersed in the mounting medium, cedar wood oil, which prevents any further change in regain of the wool [2]

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* This correction is to allow for the back pressure due to the viscosity of the liquid, given by $\frac{t_0 P}{t}$. If this is subtracted from P in any of the later equations given it will be found equivalent to subtracting t_0 from the observed time.

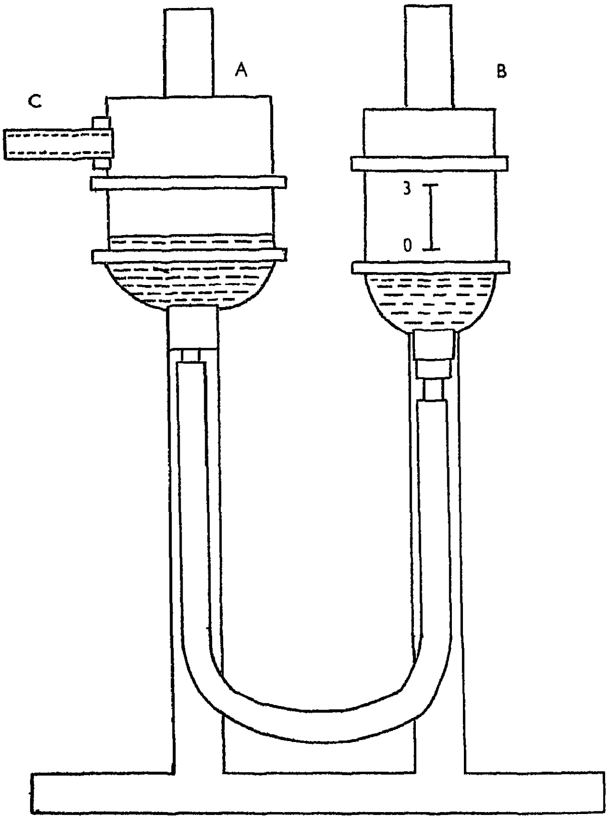

Fig 1

3. CORRECTION FOR SLIP AT THE BOUNDARIES OF THE AIR SPACES

The relevant nomenclature is repeated for the sake of completeness.

A = area of the plug cross-section.
P = mean pressure across the plug.
L = length of the plug
V = volume of the plug $= A \times L$
μ = the viscosity of air.
v = the volume of air passing in time t measured at the mean pressure (atmospheric pressure—$P/2$)
$\bar{d}$ = the mean fibre diameter determined by the microscope
σ = the standard deviation of diameter
c = the fractional coefficient of variation $= \sigma/\bar{d}$
d = the mean fibre diameter for the plug $= \bar{d}(1+c^2)$
d_1 = actual fibre diameter at any point
ρ = density of wool
M = mass of wool in the plug
k = a dimensionless shape factor
ϵ = porosity or free air space per unit volume of plug $= 1 - M/\rho V$.
S = surface area per unit volume of material

In the previous paper the relation between d and $\bar{d}$ was not considered in detail since it was assumed to be approximately constant for tops and therefore included in the shape factor However, since the diameter enters into the formula in a more complex manner when the the correction due to slip at the boundaries is taken into account further consideration must be given to this relation. In the usual derivation of the equation the diameter does not directly enter into the formula but is calculated from the surface area per unit volume, S. The complete expression for S is,

$$S = \int 4\pi\, d_1\, dl - \int \pi\, d_1^2\, dl$$

the integrals being taken over the total length of fibre in the plug.

Hence $$S = 4\int d_1\, dl \,/ \int dl - \int d_1^2\, dl \,/ \int dl = 4\,\bar{d} - (\bar{d^2})$$

where $\bar{d}$ is the length-proportioned mean diameter (as determined by the microscope), and $(\bar{d^2})$ is the similarly proportioned mean square diameter.

Hence $$S = 4/d$$

where $$d = (\bar{d^2})/\bar{d}$$

Now $$(\bar{d^2}) = \frac{1}{n}\Sigma\left\{(d_1 - \bar{d}) + \bar{d}\right\}^2 = (\bar{d})^2 + \sigma^2$$

hence $$d = \left\{(\bar{d})^2 + \sigma^2\right\} - \bar{d} \quad = \bar{d}\left\{(1 + \sigma^2/(\bar{d})^2\right\}$$

$$= \bar{d}(1 + c^2)$$

The fundamental equation given in the previous paper was originally derived for liquid flow through granular beds, and it was therefore assumed that the layer of fluid at the pore boundaries was stationary. However, when the mean free path of the fluid molecules becomes an appreciable fraction of the pore size, the thermal agitation of the molecules gives rise to slip at the boundaries and a correction must be applied for this in the same way as is done with small capillaries In the latter case this results in the flow being increased by the factor[3] $(1 + 4\lambda/a)$ where λ is the slip coefficient and is related to the mean free path of the gas molecules, and a is the radius of the capillary In the case where the pressure drop across the capillary is not negligible compared to the mean pressure the value of λ corresponding to the mean pressure is used.

Various authors[4-7] have applied this correction to flow through granular beds obtaining slightly different results and these have been discussed by Carman and Arnell [7] Rigden[4] applied the correction by employing the conception of the mean hydraulic radius as applied to the capillary, and directly transferring the results to the porous plug Carman and Arnell consider that Rigden's correction is too small and give a different correction based on those originally due to these two authors individually.[5,6]

However, Williams[3,8] has shown that the ratio of the slip coefficient to the mean free path can vary from 0·85 to 1·41 according to assumptions made in the derivation, and prefers to take Knudsen's semi-empirical value for the slip coefficient

$$\lambda = 0{\cdot}81\frac{8\mu}{3}\sqrt{\frac{2}{\pi p \rho_a}}$$

where p is the mean pressure in the capillary and ρ_a is the density of air.

Substituting for $\rho_a = p/RT$ where R has the value (in dynamic units) 2 8703 × 10⁶ for dry air, and T is the absolute temperature,

$$\lambda = 0.81 \frac{8\mu}{3p} \sqrt{\frac{2RT}{\pi}} \tag{1}$$

If this value of λ is substituted for 0 875 × mean free path in equation (10) of Rigden's paper it becomes identical with equation (8) in Carman and Arnell's paper for the particular case of $k_0 = 1{\cdot}69$, which is very close to the value obtained for triangular pores, and which is found to apply for fibrous plugs with fibres oriented parallel to the direction of flow. Knudsen's value for λ can thus be used in Rigden's equation, which, when written in the form of the previous paper for determining both d and ρ, becomes

$$M = \rho V - (M^2/t)^{\frac{1}{3}} \left\{ \frac{16k\mu v L^2 \rho}{Pd^2} \right\}^{\frac{1}{3}} \left(1 + \frac{8\lambda}{d(\rho V/M - 1)} \right)^{-\frac{1}{3}} \tag{2}$$

The relation between $(M^2/t)^{\frac{1}{3}}$ and M is thus not quite linear for a given plug and there appears to be no simple method of plotting which will give both d^2 and ρ together. The value of λ for air at normal pressure is about 0·1 micron and the curvature is sufficient to make the mean slope of the curve over the range of porosities encountered deviate appreciably from that of the straight line going through the point $(M^2/t)^{\frac{1}{3}} = 0$, $M = \rho V$.

However, if the value of the density is known or can be measured by other means the equation for the determination of d (being the positive root of the fundamental equation) becomes

$$d = \frac{4M}{\rho V - M} \left\{ \left(\frac{k\mu v L^2 \rho}{Pt(\rho V - M)} + \lambda^2 \right)^{\frac{1}{2}} - \lambda \right\} \tag{3}$$

and d may thus be found directly from the experimental values of the right hand side of the equation. The approximate per cent error in d due to neglecting λ is given by

$$\Delta d\% = 40 \frac{1-\epsilon}{d\epsilon} \tag{4}$$

which increases as the factor $(1-\epsilon)/\epsilon$ and hence as the porosity ϵ becomes small

For the most extreme conditions likely to be met with wool fibres, *i.e.* $d = 16$ microns $\epsilon = 0{\cdot}45$ this gives an error of 3 per cent Fig 2 gives this error for other values of ϵ and d.

The present section is more concerned with the determination of k from known values of d and the corrected equation for this is

$$k = \frac{d^2 Pt(\rho V - M)^3}{16\mu v \rho L^2 M^2} \left\{ 1 + \frac{8\lambda}{d} \left(\frac{M}{\rho V - M} \right) \right\} \tag{5}$$

The approximate percentage error in k due to neglecting λ is given by

$$\Delta k\% = -\frac{80M}{d(\rho V - M)} = -80 \frac{1-\epsilon}{d\epsilon} \tag{6}$$

which using the value of λ given by Knudsen's relation is 6 1 per cent. for the values of the diameter and porosity given above The error in k for other values of d and ϵ is shown in Fig. 3

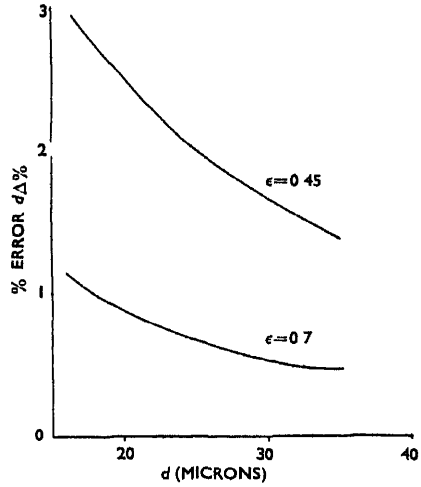

Fig. 2
Error in d due to neglecting λ.

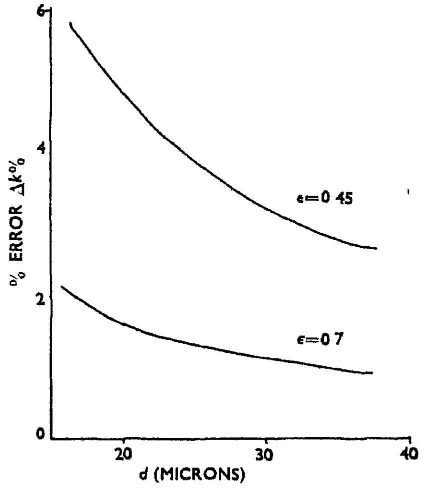

Fig 3
Error in k due to neglecting λ.

In this paper the values of d or k determined from equations (3) or (5) will be used, although the error due to neglecting λ is generally not much greater than that due to variability of results.

4. PARALLEL PLUGS

Plugs of fibres prepared such that the direction of air flow is parallel to that of the sliver, will henceforth be termed "parallel plugs". They are made by pulling one or more doubled lengths of sliver through a short brass tube by means of a loop of string. The protruding sliver is cut off flush with the ends of the tube by means of a sharp razor blade. Fibres containing oil are previously cleaned in ether and conditioned without disturbing the arrangement of fibres in the sliver.

The effect of varying the plug length was investigated in an effort to reduce the sampling variance of the results. Plugs of four different lengths between 2 and 10 cm were made and a series of 10 determinations of k was made using a top of known fibre diameter distribution Fig. 4 shows the coefficient of variation of k from which it can be seen that increasing the plug length to 10 cm gives a large reduction in variability The coefficient of variation of k due to the fibre sampling variance is negligible even for the shortest of tubes used, and the reduction is greater than can be accounted for by the reduction in experimental errors such as weighing or timing associated with a larger mass of fibres It is possible that the fibres are not uniformly arranged but occur in domains of slightly different arrangement and/or porosity and these are sufficiently large for the variance to be sensitive to an increase in tube length

Parallel plugs cannot be made with a porosity much less than 0 45 and if greater than 0·7 packing is often far from homogeneous. Within this range the shape factor seems reasonably independent of porosity as may be seen from Table I which gives the shape factor derived from experiments on 3 tops at 3 different values of porosity. Each figure is the mean of 3 results and an analysis of variance showed that the variance between porosities was not significantly different from that between different samples at the same porosity

Table I
Shape factor, *k*, from plugs of different porosities

Top	Diameter, *d* microns	*k* at Porosities. 0·684	0·578	0·470
1947B	28·3	2·01	2·04	2·07
1947C	23·6	2·06	2·07	2·08
1947D	19·5	2·12	2·12	2·06

For medullated fibres the commonly accepted value for the density of wool, 1·31, must not be used but instead the over-all density of the fibres. This may be found from the projector if fibre diameter and medulla diameter are both recorded. The correct value of ρ will then be given by:

$$1{\cdot}31\left\{1-\frac{d^2_m(1+c^2_m)}{d^2(1+c^2)}\right\},$$

where the subscript *m* refers to the medulla

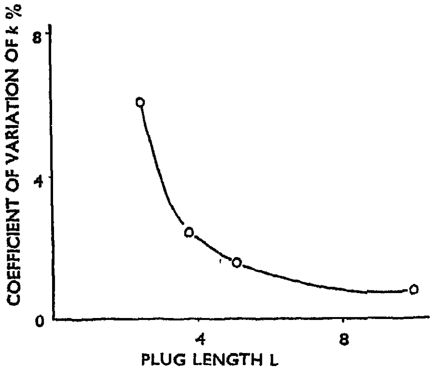

Fig 4
Effect of increasing plug length on variability of *k*

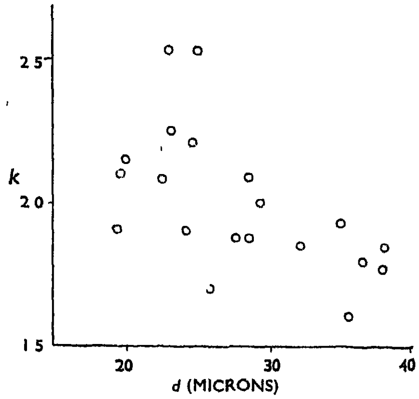

Fig 5
Variation of shape factor with top fineness for parallel plugs.

Effect of fibre arrangement

If the fibres in a sliver are all strictly parallel and reasonably circular in cross-section the pore cross-section for a parallel plug may be expected to be very little different from that of a triangle if the fibres are just touching. The corresponding value of *k* has been given by Carman[9] as 1·67 * If the fibres are not parallel the value of *k* would be different due to the change in the pore cross-section and the more tortuous paths of the air through the plug resulting in an increase in *k* as soon as the parallel arrangement was departed from. As tops vary in their degree of fibre parallelism it was thought to be responsible for the large variations in *k* often found between different tops when tested as parallel plugs. This would prevent the accurate determination of fibre diameter. Fine fibres being less rigid and more difficult to straighten by processing might be expected to show large values of *k*. That this is so in general may be seen from Fig. 5 in which are plotted shape factors for parallel plugs found from a good number of tops of varying finenesses It will be noticed that the coarsest tops give values of *k* approaching 1·67

If the value of *k* is critically dependent on fibre arrangement it was thought that its determination might provide a useful measure of fibre parallelism if

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*For fibres parallel to the direction of flow *k* is identical with k_0.

diameter was determined by other means, and experiments were carried out to see whether the test could be used in this way

To get some idea of the largest likely variations a series of determinations of *k* was made on top fibres in two ways, (1) as an ordinary parallel plug, (2) the same fibres removed from the tube cut up by scissors into short lengths, separated by hand and re-packed in a more or less random manner Table II shows the results of these tests and confirms the increase in *k* on departure from parallel arrangement.

Table II
Shape factors for different arrangement of the same fibres

Top	Fibre diameter (microns)	*k* Parallel	*k* Cut and separated
1947A	35·8	1·64	5·54
1947B	28·3	2·06	5·08
1947C	23·6	2·08	4·75
1947D	19·5	2·10	4·78

An experiment was then made to determine whether relatively small changes in fibre arrangement could be measured Three samples of nylon staple fibres were available and these provided slivers of good regularity and small variability of diameter Parallel plugs were made up with the material in the form of (*a*) card sliver, (*b*) the same gilled with a draft of 4; *k* was determined from the air flow data and the fibre diameter found from the projector. The values of *k* are shown in Table III from which it appears that the gilling process has led to a small but definite decrease in *k* in each case.

Table III
Effect of gilling on shape factor for parallel plugs

Material	Fibre diam (microns)	Value of *k* for	
		Card sliver	After gilling
5-in nylon S F.	21·5	2·60	2·27
4-in. ,, ,,	21·5	2·59	2·36
2½-in ,, ,,	21·5	2·59	2·38

The value of *k* was then determined for wool fibres of about the same diameter at different stages of top processing and the results, given in Table IV, illustrate the gradual reduction in *k* with pin treatment

Table IV
Values of *k* for parallel plugs at different stages

Material	Fibre diameter (microns)	*k*
Pre-carded wool	20—22	5.94
Card Sliver	20—22	2·35
Top	20—22	2·05
Woollen slubbing	20—22	2·68—3·06

5. PLUGS OF RANDOMIZED PIECES

It will be seen from Fig. 5 that for wool top fibres, *k* for parallel plugs ranges from 1·6 to 2·5 and this could cause differences of about 22 per cent. in the determination of diameter These data on the effect of orientation suggested that accurate determinations of diameter would be possible only by some method which destroyed the initial orientation of the fibres and reimposed some regular or random arrangement It would be difficult to do this for long fibres but some success was secured by cutting short pieces of fibres and randomizing these by shaking up in petrol ether This technique will now be described in detail

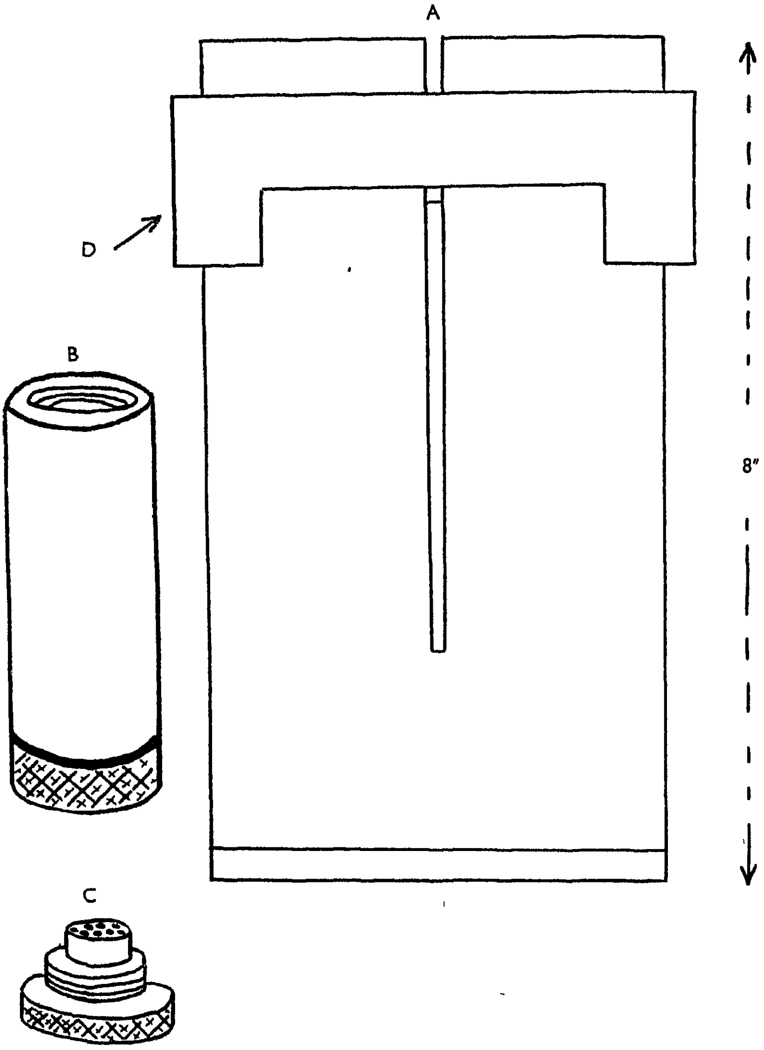

Fig. 6

The fibre pieces were prepared on the simple cutter shown at A, Fig. 6. This consists of a $\frac{1}{16}$ inch thick steel plate with a slot $\frac{1}{12}$ inch wide down the centre A slide D contains a tongue which just fits the slot The slot is first filled with top by taking lengths in two hands and pulling them down into the slot The slide is then pushed down hard and the fringe of top at each side of the plate cut off cleanly by a sharp razor blade. The fibre pieces in the slot are then pushed out and are of length about 1 5 mm The slot when full gives about 0 4 gm. of fibre and as 0 7 gm is required for one air flow determination, two fillings are used The pieces are shaken up for about 1 minute in a flask containing some 150 c.c of petrol ether This serves the double purpose of destroying their initial arrangement and cleaning them of oil, *etc* They are then decanted into a filter funnel and, when the petrol ether has drained away, are put in an open glass dish and left to condition.

The brass tube into which the fibres are packed is shown in Fig. 6, B and C. It is of nominal dimension $\frac{5}{16}$ inch internal diameter and effective length $1\frac{3}{8}$ inch. At one end it has a screw-top covered with a grille of fine holes. A second cap C screws on the other end and the upper end of this is also covered with a grille of fine holes which projects about $\frac{1}{4}$ inch into B when screwed on. The tube is accurately and smoothly finished, and its internal diameter and effective length are determined as accurately as possible.

An approximately constant porosity of 0 7 is used, and with the size of the tube given corresponds to 0 7 gram of fibre This amount of the conditioned pieces is weighed out and packed into B Packing is done carefully to ensure a bed of uniform porosity. Small amounts of fibre pieces are taken up in forceps, placed in the tube and pressed down with a smooth brass rod which just slides in The bed is pressed down in this way after each addition and masses of fibre much greater in size than the tube diameter should be divided up before insertion After the last addition the rod is removed and the cap C quickly pushed in and screwed on The plug is then placed in the apparatus and several determinations are made of the time of flow. When this becomes reasonably constant the plug of fibres is weighed to the nearest milligram

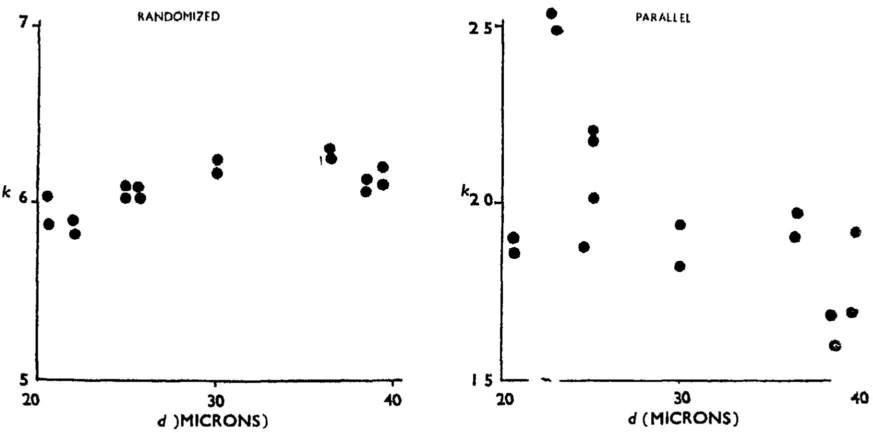

Fig 7

Fig 7 shows results obtained on 8 different tops of fibre diameters from 20 to 40 microns The derived value of *k* is shown for both randomized and parallel plugs for two determinations in each case and the results are plotted on approximately the same percentage scale The scatter is much less for the randomized plugs

Analysis of variance	d f	Mean variance	Coeff of variation %
Parallel plugs			
Between tops	7	0·1436	19·0
Between samples	8	0 0042	3 3
Randomized plugs			
Between tops	7	0 0633	4 1
Between samples	8	0 0046	1·1

The analysis of variance shows that the coefficient of variation of *k* has been reduced from 19·0 to 4 1 and this is the figure on which the accuracy of the determination of *d* depends. Two determinations of fibre diameter on a top would give an accuracy of 2½-5½ per cent. using an over-all shape factor of 6·12. However, the correlation between shape factor and diameter is significant and use can be made of this to increase still further the accuracy of determination of *d* The dependence of *k* on *d* can be incorporated in the equation to give *d* and if this is done the following empirical equation is obtained which gives about 2 5 per cent. accuracy for *d* Thus 19 out of 20 times a pair of determinations of *d* should be less than 2½ per cent from the true mean diameter of the fibres

Equation for *d* with randomised plugs at 20° C (non-medullated wool)

$$d = \frac{M}{\rho V - M}\left\{\left(\frac{2693 v L^2}{Pt(\rho V - M)}\right)^{\frac{1}{2}} - 4{\cdot}4\right\} \qquad \ldots \quad (7)$$

where *d* is given in microns, *P* is expressed in cm of water, *t* in seconds, $\rho = 1{\cdot}31$ and other quantities in CGS units.

6. ACKNOWLEDGEMENTS

We are indebted to Dr. A. B. D Cassie, under whose direction this work was carried out, for suggestions and advice, and to Mr R. C Palmer for helpful discussions. Thanks are due to the Council of the Wool Industries Research Association for permission to publish this account. Acknowledgement is made to a referee for the simplified form of equation (4).

REFERENCES

[1] Cassie, A B D *J Text Inst*, 1942, 33 T185
[2] Anderson, S L and Palmer, R. C. *International Wool Textile Organisation Tech. Comm. Proc.*, 1948, 2, 5.
[3] Barr, G *A Monograph of Viscometry* (Oxford University Press, 1931), p. 157.
[4] Rigden, P. J *J. Soc. Chem Ind*, 66, 130
[5] Arnell, J. C. *Canadian J Res*, 1947, A25, 191.
[6] Carman, P. C. *Nature*, 1947, 160, 301
[7] Carman, P C. and Arnell, J C. *Canadian J Res.*, 1948, A26, 128.
[8] Williams *Proc Roy. Soc*, 1926, 110A, 141
[9] Carman, P. C. *Trans. Inst. Chem. Eng*, 1937, 15, 150.

47—AN AIR-TEST FOR MOISTURE IN COTTON

By W Lawrence Balls

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INTRODUCTION

The number of tests made yearly by the Alexandria Testing House in Egypt began to exceed ten thousand when it was five years old. A disturbing possibility emerged during consideration of its future, to wit, that it should theoretically be prepared for development to an output whereby the whole Egyptian cotton crop was tested not once, but twice, once on arrival in Alexandria as country bales, once on departure as export bales. This would necessitate between two and three hundred thousand tests annually, and the prospect of developing to such an extent upon a basis of the slow and cumbersome procedure of oven-tests did not seem attractive. The investigation of alternative methods appeared to be worth a good deal of trouble.*

Capacitance hygrometry was first tried out,[1] succeeding up to a point, but quite failing to meet test-certificate requirements. Then a fresh investigation was started of the method here described, and by 1940 we had five sets of air-test apparatus available, each able to produce eleven tests an hour, or nearly 200,000 a year for the five. Computation and checking were also quicker, but the staff of samplers and transport workers would have remained unaltered, though all weigher's operations would have gone, so that the substitution of a six-minute test for a ninety-minute test was only a partial solution

Also, the significance of the air-test result was limited by the hysteresis loop, which brought the standard deviation up to about 0·25 per cent., or 2 50 % % approximately. This was far too large, except for an emergency. Further investigations by which it had been hoped to eliminate the hysteresis error were stopped by war work, and the method thus remains of moderate interest only.

It may be added that the speculations on possible demands which started these investigations were soon justified Nine years after beginning operations the Alexandria Testing House did nearly 200,000 tests in one year, on an equipment of eighty-four ovens The millionth test certificate[2] was issued in its fifteenth year.

THE METHOD

The air-test consisted in withdrawing air from the cotton sample (actually with re-circulation) and measuring its humidity, this being first expressed as milligrammes of water per litre of air, and then converted to relative humidity at the temperature of the cotton sample From the result of subsequent oven-tests on each sample thus examined one obtained graphs such

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* As president of the Board of Trustees of the Alexandria Testing House from its inception in 1932 until shortly before its millionth test-certificate was issued in 1947, the writer was primarily concerned with policy and anticipations The Air-Test was ready as a stop-gap had the testing-house been destroyed after Italy declared war. Fortunately we escaped serious damage, though narrowly. The achievement of full theoretical output when using the standard gravimetric methods, which had appeared to be improbable under Egyptian working conditions, was nevertheless reached through the foresight and organization of the Managers

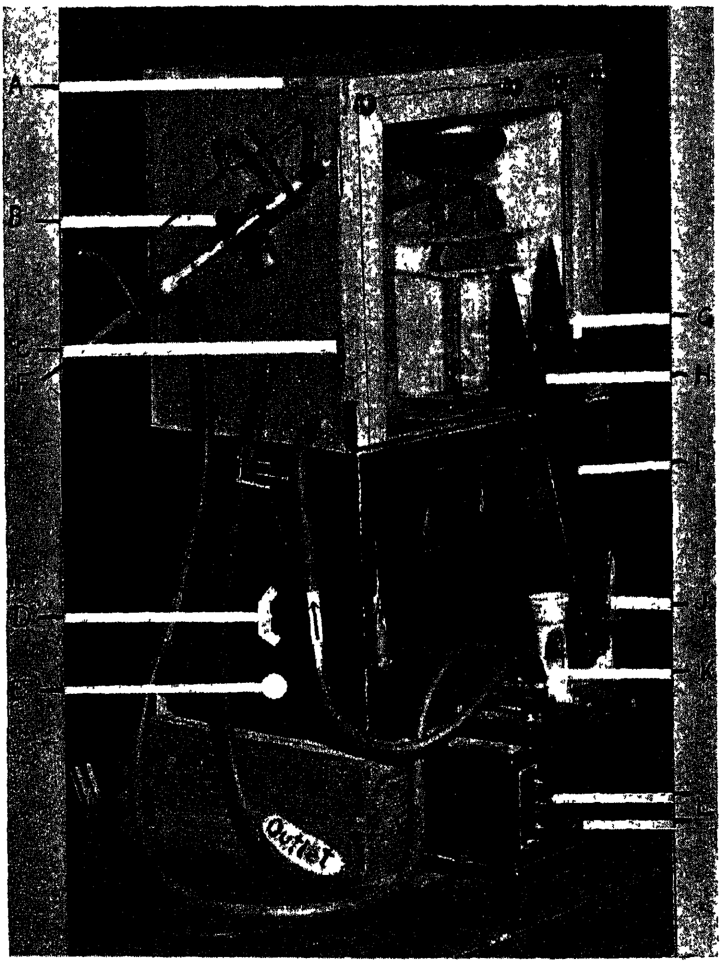
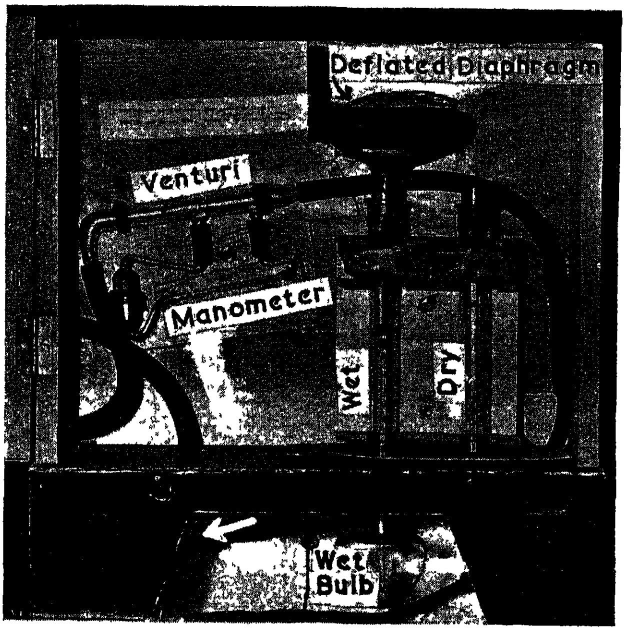


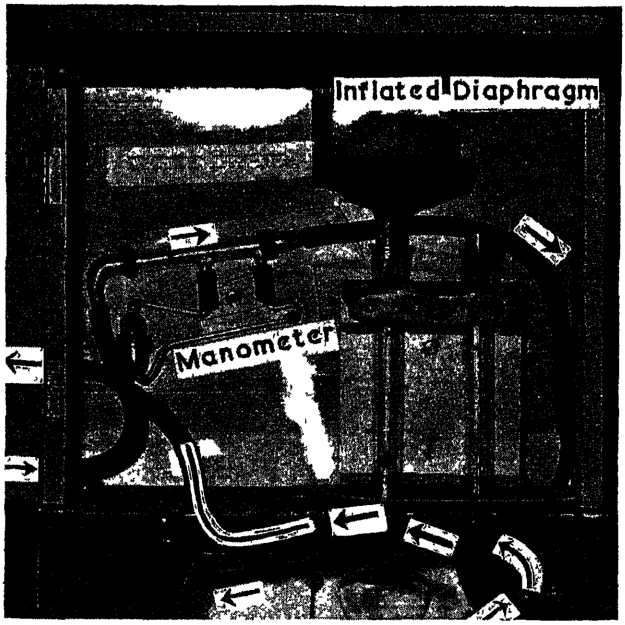
Fig 1A

Precision Wet Bulb General View

A—Roof opens, B—Lens slider for intake thermometer, C—Front opens, F—Movable intake (or outlet), D—Four turns of ¼″ copper tubing in (E) Water Bath of dilute copper sulphate, G—Three point slider for dry-bulb lens, H—Three-point slider for wet-bulb, I—Sheet metal legs of cupboard, fitting over water-bath, J—Counter-weight for dry-bulb lens, K—Two-minute sand-glass, L—Speed Control Switch of pump



Apparatus idle, with wet bulb resting in reservoir of mercuric chloride, the diaphragm being deflated, and the manometer of the venturi meter at zero



Apparatus working Air passes through the venturi, raising its manometer reading to the value required, then downwards to the left, through the copper coil in the water-bath. Leaving this it passes over the dry bulb and then over the wet bulb, which has been raised by inflation of the diaphragm Emerging from the water-bath it leaves the casing on the same side by which it entered

Fig 1B

FRONT VIEWS, WITH GLASS DOOR WHICH CARRIES READING LENSES SWUNG OPEN.

as Fig 3, showing the relation between moisture content of the cotton and the relative humidity of the air inside it.

The technique has two components. The first is the method for measuring the moisture content of the extracted air, which has been described elsewhere,[4] and so need only be summarised here, with the addition of unpublished illustrations (Fig 1) The second is the method for extracting the air from the cotton, and for measuring the temperature of the cotton, this latter is the principal object of this note, but we shall not attempt to do more than indicate the complications of moisture and temperature which had to be studied.

Outline of the Hygrometer Design.

Certificated mercury-in-glass thermometers used inside a limited range of temperature are very dependable over long periods, and for this reason the wet-bulb was used in preference to other methods more liable to zero-shift.

Air extracted from the cotton, and returned to it through a diaphragm pump (Fig 1) with speed control, was passed through a coil of small copper tube immersed in a ten-litre water-bath at room temperature. The bath could be warmed if necessary, but was not thermostatic. Also immersed in this bath were two inter-communicating stoppered glass tubes, containing each a quick-response thermometer (of sling-psychrometer type) which was read to estimated tenths of one degree Fahrenheit by an anti-parallax lens

The tube containing the wet bulb was expanded below into a reservoir filled with 0·1 per cent. mercuric chloride The use of this dilute antiseptic instead of distilled water is a most important detail. During routine use of the apparatus in these highly critical determinations it was found that the well-known deterioration of the wet-bulb wick was so much accelerated in summer-time that it could be detected after one day's use, suggesting a biological causation The remedy is so effective that a wick which had stood idle in the apparatus for four years gave normal readings when brought back into use. Occasional additions of distilled water made good evaporation losses

The wick was a braided cotton sleeve just covering the bulb and normally immersed in the reservoir, but the thermometer was lifted automatically into position for exposure and reading by air-pressure acting on a flexible diaphragm when the pump was started The air coming from the copper tube impinged on the dry-bulb, then on the foot of the lifted wet-bulb, leaving it opposite the top of the wick in a condition of extreme turbulence, and at a known velocity of 6 metres per second determined by the size of stainless steel inlet and exit liners, and by measurement through a venturi throat with its mercury manometer which was included in the air circuit.

Fixing the air-discharge on the pump control at 6 litres per minute by the indications of the venturi meter standardised the air-speed as well as the condition of the wick Readings made to 0 1° F. gave open-scale values to the nearest 0·5 per cent R.H. when room temperatures were around 70-80° F , the scale could be opened out for lower room-temperatures by warming the water-bath Constant reading of temperature was reached within two minutes, which were timed with a sand-glass; if the times are noted on a clock-face there is liable to be mental confusion with the numerical values of the thermometer, and consequent needless fatigue. The temperature drift of the dry bulb (*i.e.* of the water-bath) was very slow and therefore self-checking

Computation was graphic, by needles pricked into a cork-backed chart enlarged photographically from that published by the Carrier Engineering Co. On this the milligrammes per litre determined by the hygrometer readings were converted to relative humidity in the cotton by a second needle

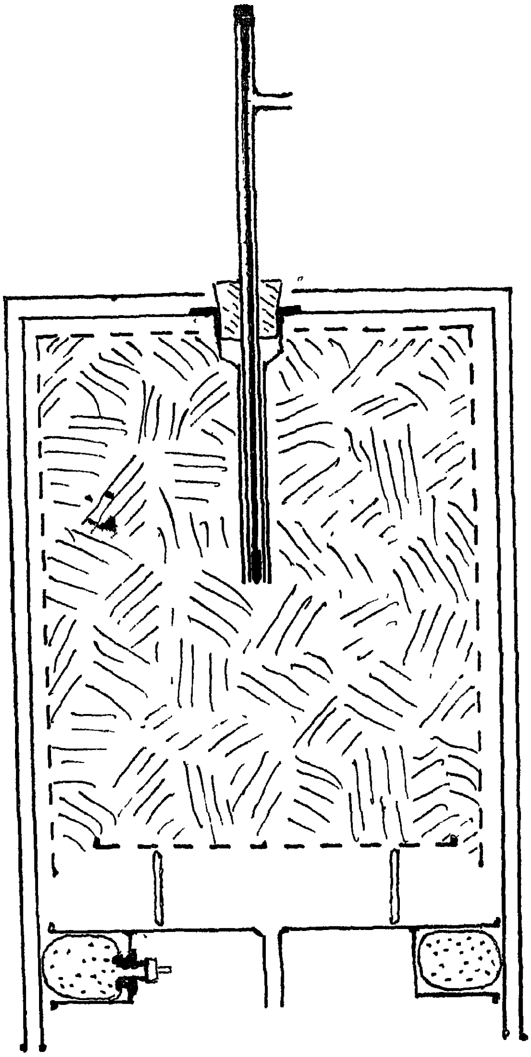


Fig 2 Section of tin box in the inverted position for testing Shows cotton contained in perforated lining within the double wall, long thermometer in sheath, and pneumatic washer below

pricked in when the third temperature, that in the cotton, had been ascertained It should be noted that the precise formula employed for converting bulb differences to relative humidity is immaterial, so long as it is always the same, within the narrow requirements of a testing house's matching of readings to the cotton content Jellinck's tables were available, but the Carrier graph was convenient

Arrangement and Treatment of the Cotton.

A cylindrical box (Fig. 2) rather more than a foot high and eight inches in diameter was provided with a "pneumatic washer" as a lid. It was all arranged to weigh as little as possible for experimental purposes, though weightiness is immaterial for routine testing. This pneumatic washer is a convenient way for sealing at any level in the tin; a shortened bicycle inner tube with valve lay in the periphery of a flanged tin cover which would drop freely into the tin box and on to the cotton placed inside, a lead weight placed on the washer gave fairly constant compression to all samples. A few strokes from a bicycle pump inflated the tube, thus sealing the clearance between the washer-flange and the wall of the box In the five washers as actually made and used there was a constructional defect which risked occasional slight leakage of air, and consequent error, this defect lay in the fact that although the tin-work was made smooth at its seams, and the joint in the rubber tube was bevelled, yet the latter did not always lie perfectly flat and was thus liable to a tiny leak which might bring a trace of room air into or out of the system. Rubber tubes vulcanised without a lap joint, or with a seam running round the upper or lower side, were the obvious requirement, but were unobtainable locally at the time they were needed

The fixed end of the box was perforated centrally and reinforced with a flange to take a rubber cork This cork carried a long glass tube with a side inlet, and a long quick-response thermometer in its middle, the bulb was protected by a thin-walled Duralumin tube extension of the glass tube The flanged hole led into a Duralumin tube slightly larger than the thermometer holder, projecting into the centre of the box Thus when the box was filled with about half a kilogram of cotton (the usual size of sample) the bulb of the long thermometer could be slipped in to the centre of the mass, with very little metal round it, and with a free air-way past it through the glass tube, to or from a nozzle in the centre of the pneumatic washer

The whole box was contained permanently in another one slightly larger, with quarter-inch clearance set by small rubber blocks, forming a double jacket for better thermal insulation when being handled. After filling with cotton and sealing pneumatically, the double-walled box was inverted (Fig. 2) on a low stool so that pressure tubing could be connected from the nozzle in the centre of the washer to one side of the hygrometer unit, while the other side was similarly connected to the side tube of the long thermometer casing By so connecting that air was sucked past the bulb from the centre of the cotton one should initially obtain its temperature This temperature would change, of course, towards the temperature of the water-bath on prolonged running, were it not for the Masson effect produced by the few milligrammes of water evaporated from the wet bulb, which causes the cotton to generate heat through absorption

This Masson effect, small though it was, almost nullified the great advantages of the wet-bulb technique. With the connection made as just described there was a rapid concentration of this water, giving false temperature as well as false humidity

Eventually a satisfactory routine was obtained by compromise Inside the box was added an inner lining of perforated and corrugated thin metal, which extended over the fixed end, as well as being formed into a loose cover under the pneumatic washer (Fig 2) Air could then freely enter or leave the mass of cotton over its whole outer surface. A two-minute run was first made with the wet bulb thermometer prevented from making its automatic rise into the air-stream, with connections made so that the air was flowing from the outside to the centre of the mass. This run provided the temperature of the cotton. Then the connections were reversed, and the wet bulb released to function for another two-minute run. Now the Masson effect was localised where the air entered in the centre of the mass, but the air thus warmed had a slow and long passage through an expanding path to its emergence all over the outside of the mass, and so had a water-content in equilibrium with the outer layers.

It should be noted that the hygrometer unit and the tube leads contained less than 1 per cent of the volume of air in the cotton, and that the latter was about the same as the volume of air pumped per minute, as fixed at the venturi gauge. No difficulty was found in getting reasonably uniform packing of the cotton in the few seconds which might be allowed to elapse between opening the sealed and air-tight sample container and replacing the pneumatic washer, any such exposure is a source of error The operator used rubber gloves in sweaty weather

RESULTS OF TESTING

Using the method of flow-reversal as described, some long series of dual observations were specially fitted into the routine of the Alexandria Testing House as works' trials, all incoming samples being air-tested by Mr. S. Blattner on their way to the oven-test. The results from the last series obtained before the interruption of war are plotted in Fig 3. A few points appear to be slightly distorted by the small and erratic leak at the pneumatic washer tube-joint, already mentioned, but the general result is tolerably good. Evidently it would be much better if hysteresis could be eliminated; the standard error of any one determination is approximately 2·5 % %, about a dozen points lie well clear of the dotted lines which indicate the twenty-to-one chance of ±5¼0 % %, and these are mostly suspect on the available records of room-air conditions

A test showing this degree of uncertainty through hysteresis is more usable in working practice than would be apparent at first sight, provided that it is free from drift, and also cheap and quick We had no drift, the five sets cost £80 in all during 1939 apart from our labour in making up components, and Mr Blattner did eleven tests an hour for three or four hours at a sitting without undue fatigue The various errors in the procedure of moisture testing have been discussed in an Alexandria Testing House duplicated paper, and the following excerpts about ascertained standard deviations are relevant to a possible use of the air-test, even in its present imperfect form·

(*a*) S D. of oven-test itself on identical samples	1 04 % %
(*b*) S D. of different samplers on the same bale	2 14 % %
(*c*) S D. of contents of country bales in the same "lot"	4·16 % %

The combination of (*a*) and (*b*) gives 2 40 % % for the oven-test result derived from different samplers drawing from the same bale Further combining this with (*c*) gives an S.D of 4 80 % % for the test result on any one country bale in a "lot"; the bale-to-bale variability dominates the situation, and can be reduced only by sampling from more bales Under the international agreements for testing procedure with cotton the samplers take one bale at random out of every ten for oven-tests. Their work would be nearly doubled if two bales were taken, but the use of the air-test would effect a compensating reduction at the other end by eliminating the weighing balances and the oven-room Substituting for (*a*) the much bigger 2·50 % % of the air-test, but dividing (*c*) by the square root of two, the re-calculated combination of errors is substantially the same as before, with the advantage of fuller sampling from the smaller lots.

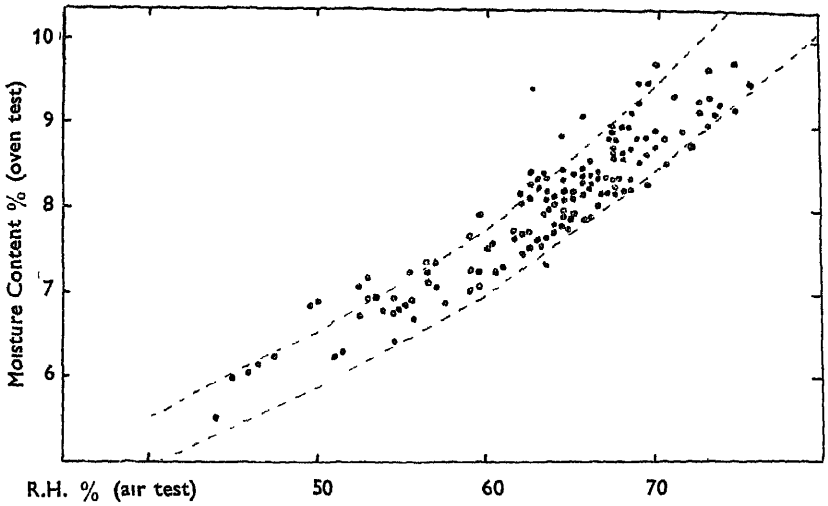


Fig. 3 DUPLICATED TESTS ON ROUTINE SAMPLES OF THE ALEXANDRIA TESTING HOUSE. Air-tested by S Blattner before passing to the oven rooms, June, 1940 Time taken was 16 hours, including some luncheon breaks, for 140 tests

Dotted lines represent 5%% deviation from the mean of the hysteresis loop as shown on p 30 of "Studies of Quality in Cotton," and so corresponed to the 20-1 chance for an S D. of 2·5 %%. Since the S.D. of the oven test at 1 04 must be compounded with that of the air test in this diagram, it follows that only 10 dots in 140 exceed this error for the air-test, a structural defect may have caused some of them

Copied from duplicated "Monthly Reports of Laboratory Research Committee," Giza 1940, p 192

My thanks are due to my colleagues the Trustees, and especially to Mr. D. A Newby, of Hewat Bridson and Newby, the chartered accountant managers of the Alexandria Testing House All possible assistance was given as usual by the works superintendent, Mr E. Gonzi, and his staff. The help in experiment provided by Mr. S Blattner as a special assistant was most valuable, both at the Cotton Research Board in making up the five sets of apparatus from components, and at Alexandria in systematic trials.

REFERENCES

[1] Balls, W L *Nature*, 1932, 130, 935 and 1933, 131, 329
Balls, W. L "Capacitance hygrometry on bales of cotton", *Egypt Govt. Min. Agric., Tech Paper*, 1934
[2] *Alexandria Testing House Progress Report*, 1947.
[3] Balls, W L "Precision hygrometry with a wet bulb." *Nature*, 1943, 152, 389

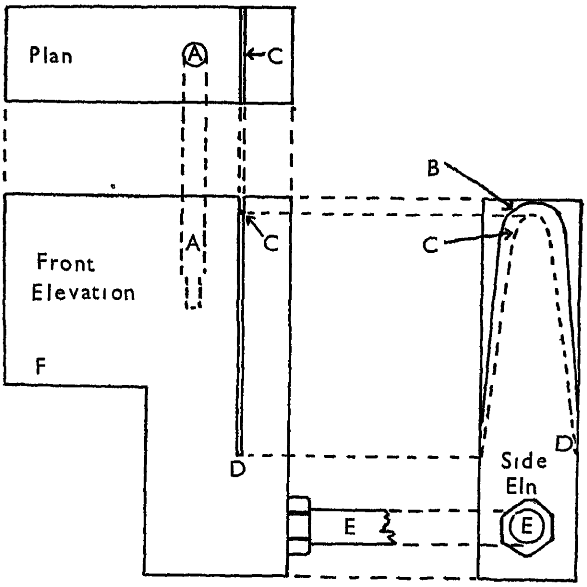
Received 21/6/49

Letters to the Editor

THE TEMPERATURE OF CONTRACTION OF FIBRES AS AN AID TO IDENTIFICATION

It has been known for some time that Vinyon fibres placed in very hot water contract to a small part of their original length. Aside altogether from the textile significance of this special property, it provides a unique means of identification since there are now no other fibres which behave in this way at this temperature. Many of the new synthetic fibres also have this property of contracting when heated. It was thought to be probable that the temperature at which the contraction occurs (in the case of non-crystalline fibres like Vinyon this appears to correspond to the second order transition point of the polymer[1]) would be a useful index to the kind of fibre present.

To measure the temperature of contraction a simple means was required of heating the fibres to a known temperature whilst observing the changes of length in them. A simple apparatus was made for this purpose.



After some trials a metal block was designed to measure the contraction temperature of fibres. It was machined from a copper casting to the shape shown in the figure. The dimensions of the block are not in any way critical, but those indicated have been found convenient in use. The shape and general dimensions were chosen to prevent any direct heat reaching the fibres from the burner used to heat the block. This is an important precaution.

The block is drilled to provide a thermometer pocket, A, about 3 cm deep and at B is shaped to a smooth curve as shown. At C there is a groove about 1·5 mm wide and 4 mm deep at the top, which tapers off in depth to nothing at D. The groove is symmetrical on both sides.

In use the block is clamped in the boss of a retort stand by the mild steel rod E which is screwed into the block and made firm there with a lock nut. The boss is adjusted to a convenient height so that the overhanging portion of the block, F, can be heated with a bunsen flame. A little medicinal paraffin oil is placed in the thermometer pocket before inserting the thermometer to provide good thermal contact with the metal of the block. The fibres to be tested are passed over the block and laid in the groove. A situation free from draughts should be chosen and heating of the block begun The temperature should be noted at which contraction, or as the case may be, melting takes place. It is convenient to do a quick test in the first experiment to get the approximate temperature and then to cool a little and repeat with slow heating near the contraction temperature. In this way the temperature can be observed to within a few degrees With a few fibres with contraction points at temperatures near the melting point there is a tendency for the fibres to stick to the block and to hinder the contraction. If it is seen that there is any tendency to stick, the fibres should be momentarily pulled away from the surface and then allowed to fall back in the groove again Carried out in this way the following results were obtained

Fibres or monofil	Contraction temperature °C	Melting point °C
Vinyon	80/3	200/10
Rhovyl	90	200/10
Pe Ce	100/10	200/10
Vinyon N	140/5	190/200
Saran	145/55	150/60
Perlon U	none	170/5
Fortinese	225/30	245
Terylene	235/40	250/5
Nylon	none	240/50
Wool	240	chars
Silk	none	chars
Orlon	none	chars

The table shows that there are now large differences between the different fibres in respect of their contraction and melting behaviour In the future new fibres may become available with properties intercalated between these so that the differences may become less distinctive, but nevertheless the contraction and melting point temperatures will be useful for identification. Properties such as molecular weight affect these temperatures somewhat,[1] and it may be expected that new fibres which have not yet reached their final development may be somewhat changed, and as a consequence their shrinkage and melting point temperatures may vary a little from those shown in the table, but at present there are such large differences between most fibres that this should not cause serious confusion

REFERENCE

[1] Schmidt and Marles *Principles of High Polymer Theory and Practice.* McGraw Hill, 1948, p 180 *et seq*

J. M. PRESTON.

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A MICROSCOPICAL EXAMINATION OF WORN TEXTILE ARTICLES

J. Text. Inst., 1949, 40, T449-T480.

It has been brought to the notice of the writer of the above paper, that certain statements in it have been, or can be, held to imply that a low fluidity in cellulose textiles is relatively unimportant; or that its importance is less than had previously been supposed. None of the results reported in the paper justifies such a conclusion, and if any part of it has been interpreted in this sense some further comments are necessary.

Earlier workers have submitted cotton yarns of simple construction to progressively more drastic chemical treatments under the most uniform conditions attainable in careful laboratory work. The resulting materials show a progressively rising fluidity accompanied by a progressively falling breaking load. By means of a scale constructed in this way it becomes possible, with certain reservations, to say that a given fluidity "accounts for" or "corresponds to" a certain percentage loss in breaking load. The scale permits a fluidity measurement to be converted into an "equivalent loss in strength", or what may be called a "chemical deterioration".

The merit of this procedure is that it enables "fluidity" to be translated—for the benefit of the technically uninformed—into the more familiar concept of loss in strength, or "tendering". Its disadvantage is that the scale of equivalence between fluidity and loss in strength is in a sense an artificial one. Under actual conditions, the chemical treatment of cotton goods may not be uniform, and the chemical attack may be localised; the very construction of the textile material may militate against uniformity of access to the chemical agent. When the chemical attack is very localised, the fluidity measures its *average* intensity, whilst the strength is determined by its *maximum* intensity. The scale of equivalence obtained from laboratory experiments designed to secure uniform treatment would then no longer apply. In the sense in which the words are defined above, the fluidity would no longer "account for" the tendering, and the "chemical deterioration" would appear small compared with the actual loss in strength.

Further, shirts, sheets and other articles are not under actual conditions broken on a testing-machine immediately after bleaching or laundering. They are submitted to complex "conditions of wear" that produce a variety of mechanical effects in the fibres before tensions applied in service cause their breakdown. It cannot be assumed that, if breaking loads were measured only after the samples had been subjected to some ideally constant mechanical treatment closely imitating "conditions of wear", the same relation would be obtained between fluidity and percentage loss in strength as when strength tests are made without previous mechanical treatment. To study the mechanical effects of wear on the fibres, and to devise a machine to imitate them, were primary objects of the investigation described in the paper under discussion.

The fluidity of cellulose fibres should be regarded as an important fundamental property in its own right. Other things being the same, the textile qualities will be the better preserved the smaller the rise in fluidity during bleaching, laundering, and other chemical processes. This statement need no longer be justified by reference to measurements of breaking load carried out on laboratory specimens. It is justified in a much more impressive way by many years of industrial experience in the use of "fluidity control".

GLADYS G. CLEGG.

The British Cotton Industry Research Association.

SOME OBSERVATIONS ON THE INFLUENCE OF FABRIC STRUCTURE ON FELTING

In the current issue of the *Journal*, there appears a letter on the above subject from Mr. Hill and Mr Kornreich (British Launderers' Research Association). This is a subject of particular interest to students of fabric behaviour and is one which, whilst not having had the publicity it deserves, has not escaped the attention of research workers in the past. The phenomenon has been investigated in this laboratory and the following added information will be found to be of interest.

Examples of felted rayon fabric have been met from time to time. About 15 years ago it was noticed, by Courtaulds' technologists, that sheetings made from viscose spun rayon felted after repeated launderings, if they were woven with a twill weave, whilst the same yarn in a plain weave did not felt. No satisfactory explanation was put forward for this behaviour

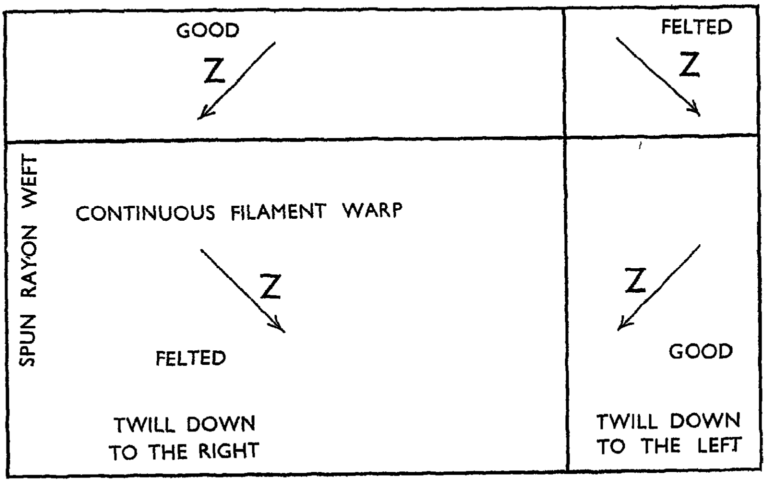
Felting is a function of the mobility of the fibres and yarns in a fabric; this is clearly understood, but felting cannot take place on a fibre with a perfectly smooth surface. Therefore, when a fibre or yarn moves there must be a factor which permits movement in one direction whilst retarding it in the other. A fabric which, in its newly woven state, does not felt, and then as a result of continued use involving mechanical and other treatments begins to show felting, must have undergone a modification involving changes to the surfaces of adjacent fibres.

With severe mechanical abrasion the surface of a rayon fibre can be so broken up as to produce a distinct "barbed" effect, this effect is accelerated when the fibres are in a swollen state. Therefore when a "barbed" character has been developed on a damaged fibre, it is likely that a fabric would commence to felt, provided there is also fibre and yarn movement at the same time, but in spite of fibre/yarn movement, felting cannot commence until some "barbs" are developed.

At the request of B.L.R.A. in December, 1947, a partially felted rayon tablecloth was examined in this laboratory.

The tablecloth was a particularly interesting example of felting since its design and construction gave a variation in twist/twill relationship. It was a border dobby satin faced cloth, woven on a continuous filament viscose rayon warp, with a spun viscose rayon weft. In two portions in which the twill ran downwards to the right, felting had occurred; in the other two portions with the twill in the opposite direction, felting had not occurred.

The cloth can be represented diagrammatically as:—



In the felted areas the twill was *down-to-the-right* and in the unfelted areas the twill was *down-to-the-left* The yarn was Z twist.

Microscopic examination revealed that the continuous filament warp was barbed to a small degree, whilst the spun rayon weft showed a more pronounced "barb" The attached photomicrograph shows this effect A photograph of a portion of a felted and unfelted yarn is also included, both are taken from the actual tablecloth

That the continuous filament yarns were not felted may be regarded as evidence that without fibre/yarn movement, felting cannot take place, even with fibre surface damage The spun rayon had felted in certain areas because there was more fibre/yarn movement in one area than another, although there was fibre surface damage all the way across the weft Thus, the only apparent difference in the pairs of areas, being a difference in the direction of twill, it was concluded that when the twist lay across the twill greater freedom of fibre/yarn takes place when the cloth is subjected to severe laundering conditions

Since this particular investigation, spun rayon fabrics with varying twist/twill relationship have been woven to provide materials for study of the general problem, which study continues in this laboratory

The writer wishes to express his thanks to Dr Whittaker, Mr John Boulton and the colleagues with whom this interesting phenomenon has been discussed

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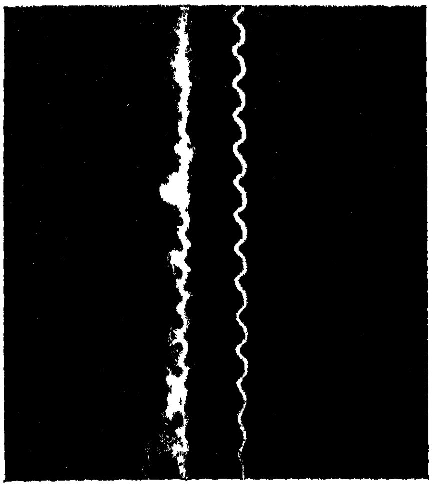
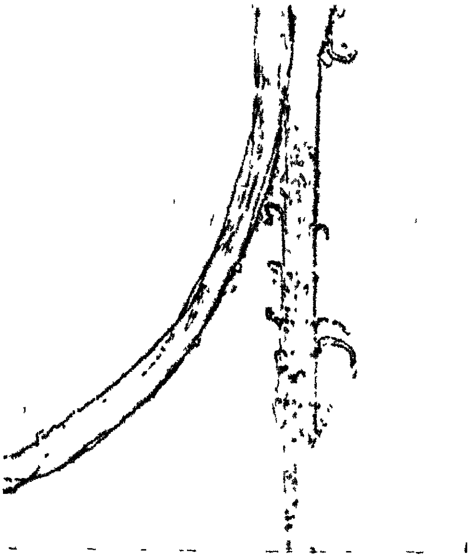


Photograph showing damage and undamaged portion of spun rayon weft



Photomicrograph of a "barbed" filament

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TRANSACTIONS

48—THE FRACTIONATION OF STARCH
Part III—THE AMYLOSE-IODINE REACTION

By R. S. Higginbotham

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By the use of a much wider range of iodine concentrations than has been used hitherto it has been shown that the absorption of iodine by amylose does not reach a limiting value other than that imposed by the limited solubility of iodine. The view of other workers that the absorption takes place in two stages has, however, been confirmed. In the first stage there is no simple relation between the amount of iodine absorbed and the free iodine concentration but in the second stage the amount of iodine absorbed is a linear function of the logarithm of the free iodine concentration. During the first stage the absorption spectrum of the absorbed iodine remains constant but as soon as the second stage is reached it begins to change in such a way as to suggest that the additional iodine is being forced into amylose helices which already contain iodine

Amylose-iodine complexes can be formed either by the interaction of iodine vapour and dry amylose in the V-configuration, for example, amylose which has been precipitated by butanol,[1] or in solution. The structure of the first type of complex has been investigated by X-ray diffraction and optical methods.[2] The results suggest that the amylose molecules have a helical configuration with about six glucose units per helix turn and that practically all the iodine is accommodated within the helices in the proportion of approximately one iodine molecule to six glucose units. Stein and Rundle,[3] postulating that the interaction between iodine and amylose is of a dipole nature, demonstrated by calculation that the stability of the complex would be expected to increase with increasing helix-length. They consider that the stabilisation energy is probably derived mainly from electrostatic and Van der Waals forces, but that the resonance contribution may be more important than the calculations imply.

Investigation of the complex formed in aqueous solution is complicated by the influence of the iodide ions which are invariably present. Bates, French and Rundle[4] observed that when iodine was added to a solution of amylose containing iodide, the activity of the free iodine remained very low and fairly constant until the amylose had absorbed from 16 to 20 per cent of its weight of iodine, depending upon the iodide concentration. At the lowest iodide concentration (0·005N) the proportion of iodine absorbed before any appreciable rise in the activity of the free iodine occurred was about one molecule to 6·5 glucose units (24 per cent.), after correction for the presence of 15 per cent. of amylopectin. From this observation, and from measurements of the absorption spectra[5] and streaming birefringence[6] of solutions of amylose containing iodine, the conclusion was drawn that the structure of the amylose-iodine complex in solution is similar to that of the anhydrous complex. The fall in the amount of iodine absorbed with rising iodide concentration was attributed to the partial replacement of molecular iodine by tri-iodide ions.[5]

The stabilities and absorption spectra of the iodine complexes of amyloses differing in molecular size have been shown to be related to the degree of polymerisation of the amyloses; hence it has been deduced[7,8] that the whole chain of iodine molecules and iodide ions in any amylose helix forms a single resonating unit. Gilbert and Marriott,[9] however, think that the resonating units are small groups of the type $3I_2 \cdot 2I'$ when the amount of iodine absorbed is very small (0·5 per cent. or less).

The purpose of the present investigation was to examine the reaction between pure amylose, iodine and iodide in aqueous solution over a range of iodide concentrations and the widest possible range of iodine concentrations, for hitherto only a small range of iodine concentrations has been covered Previous investigators, with one exception, have not employed pure samples of amylose, and although amylopectin acts merely as a diluent at very low iodine concentrations, at higher concentrations it absorbs considerable amounts of iodine. Consequently the iodide content and absorption spectrum of a complex prepared from an impure amylose may differ considerably from those of a complex prepared under the same conditions from a pure amylose and having the same content of iodine.

DETERMINATION OF THE COMPOSITION OF COMPLEXES FORMED AT MODERATELY HIGH CONCENTRATIONS OF IODIDE

The differential potentiometric titration apparatus employed has been described in Part I of this series of papers[10] and since the work was completed Gilbert and Marriott[9] have described a very similar piece of equipment. The amounts of iodine absorbed by potato amylose at 25° C have been determined for free iodide concentrations ranging from 0·002N to 0·05N and for free iodine concentrations ranging from 10^{-6}N to $1 \cdot 5 \times 10^{-2}$N. The amount of amylose in each test solution was so chosen that the amount of iodine absorbed was never less, and was usually much greater, than two-thirds of the total amount of iodine present After equilibrium had been reached the solution, containing predetermined amounts of amylose, iodine and potassium iodide, and adjusted to *pH* 4, was placed in one vessel of the titration apparatus and a control solution whose iodide concentration was as nearly as possible the same as the free iodide concentration of the test solution, but which contained no amylose or iodine, was placed in the other vessel An iodine solution, having the same concentration in free iodide as the control solution was then gradually added to the latter until there was no potential difference between the electrode in the test solution and that in the control solution. The control solution and the iodine solution were also adjusted to *pH* 4.

Let $[I']_c$ and $[I']_t$ be the concentrations of iodide ions, $[\Sigma I]_c$ and $[\Sigma I]_t$ the concentrations of total free iodine, $[I_2]+[I'_3]$, and $(I_2)_c$ and $(I_2)_t$ the activities of molecular iodine in the control and test solutions respectively when the P.D. between the two electrodes is zero. Then for a single electrode

$$E = E_0 + \frac{RT}{2F}\log_e\frac{(I_2)}{(I')^2} \ldots\ldots \quad (1)$$

where () denotes activity, and [] concentration.

When there is no difference in potential between the electrodes

$$\frac{(I_2)_c}{(I_2)_t} = \frac{(I')^2_c}{(I')^2_t} = \frac{[I']^2_c}{[I']^2_t} \text{ when } [I']_c \simeq [I']_t \ldots\ldots \quad (2)$$

Now $$\frac{(I')\,(I_2)}{(I'_3)} = K$$

hence $$\frac{(I_2)_c}{(I_2)_t}\,\frac{(I')_c}{(I')_t}=\frac{(I'_3)_c}{(I'_3)_t}$$

and $$\frac{(I_2)_c\cdot[I']_c}{(I_2)_t\cdot[I']_t}=\frac{[I'_3]_c}{[I'_3]_t} \text{ when } [I']_c \bumpeq [I']_t \text{ and } [I'_3]_c \bumpeq [I'_3]_t \quad \ldots\ldots\ldots\ldots\ldots(3)$$

When $(I_2)_c$ and $(I_2)_t$ are small compared with $[I'_3]_c$ and $[I'_3]_t$, $[I']_c \bumpeq [I']_t$ and $[I'_3]_c \bumpeq [I'_3]_t$, then $[I'_3]_c/[I'_3]_t$ can be taken as equal to $[\Sigma I]_c/[\Sigma I]_t$ without appreciable error and hence

$$[\Sigma I]_c/[\Sigma I]_t=[I']^3_c/[I']^3_t \ldots\ldots\ldots\ldots\ldots(4)$$

Table I

Amylose concentration (g /100 ml. solution)	[I′]	(I$_2$)	Concentration of total free iodine	Grams of iodine bound per 100g amylose	$\frac{C_{I'}}{C_I}$*
	(Equivalents/litre)				
0·214	0 049	0·000394	0·0151	25 0	0 81
0·120	0 01028	0 00131	0·0114	27 4	0·47
0·222	0 00975	0·000454	0·00378	26·4	0·51
0·0397	0 00228	0·000479	0 00129	26 7	0 39

$$^*\frac{C_{I'}}{C_I}=\frac{\text{Equivalents iodide bound by amylose.}}{\text{Equivalents iodine bound by amylose.}}$$

When the amount of iodide absorbed was not negligible, the activities of the molecular iodine in the control and test solutions respectively were determined by the method of Jones and Kaplan,[11] and $[I']_c$ and $[I']_t$, and hence the concentrations of free iodine in the test solution and the amounts of iodine and iodide absorbed by the amylose, were calculated by means of equations 2 and 3. If the amount of iodide absorbed by the amylose was small compared with the total amount present, the concentration of free iodine could be calculated from the potentiometric data alone, by using equation (4). When the amount of iodide absorbed could not be neglected even though $(I_2)_t$ was too small to measure, the concentration of free iodine could still be calculated by successive approximation from equation (4), provided that the ratio ($C_{I'}$=equivs. iodide bound/C_I =equivs. iodine bound) had been previously determined for the particular concentration of iodide present, for, at a given iodide concentration $C_{I'}/C_I$ appears to be substantially constant irrespective of the amount of iodine bound. (See below.)

Over the range where it could be measured accurately (24-27 per cent. of iodine bound), $C_{I'}/C_I$ increased with increasing free iodide concentration. (Table I.) Gilbert and Marriott[9] have obtained approximate values for $C_{I'}/C_I$ for complexes containing very small amounts (0·5 per cent. or less) of iodine by measuring the free iodine activities at constant iodine absorption but variable iodide concentration. When $C_{I'}/C_I$ is plotted against $\sqrt[3]{[I']}$ for the present data (Table I) or $\frac{1}{2}(\sqrt[3]{[I'_1]}+\sqrt[3]{[I'_2]}$* for Gilbert and Marriott's data, all the points lie on or very near a straight line (Fig. 1), which suggests that $C_{I'}/C_I$ is independent of the amount of iodine bound At the highest iodide concentration examined, when the complex was completely precipitated at very low concentrations of iodine, $C_{I'}/C_I$ considerably exceeded the value (0·5) which corresponds to absorption of all the iodine in the form of tri-iodide ions. When the iodide concentration was 0·01N or less the complex was either not precipitated at all, or else only at the highest concentrations of free iodine. It may be significant that under these conditions $C_{I'}/C_I$ was less than 0·5.

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*$[I'_1]$ and $[I'_2]$ are a pair of iodide concentrations for which the iodine absorption was adjusted to the same value by altering the free iodine concentration.

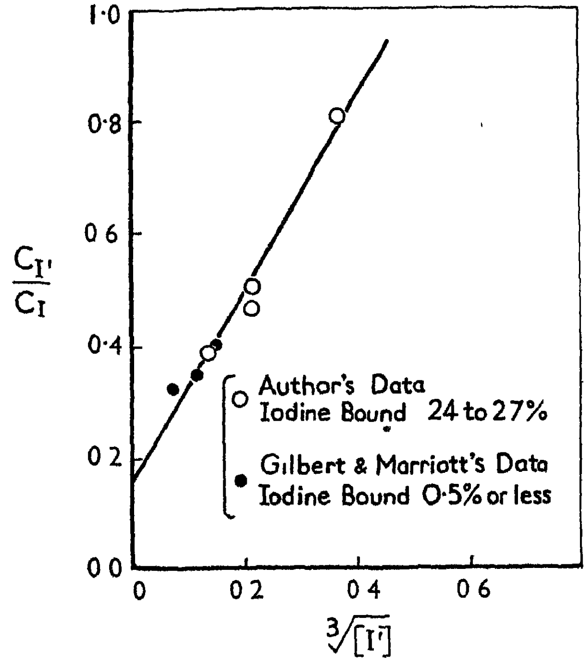

Fig. 1

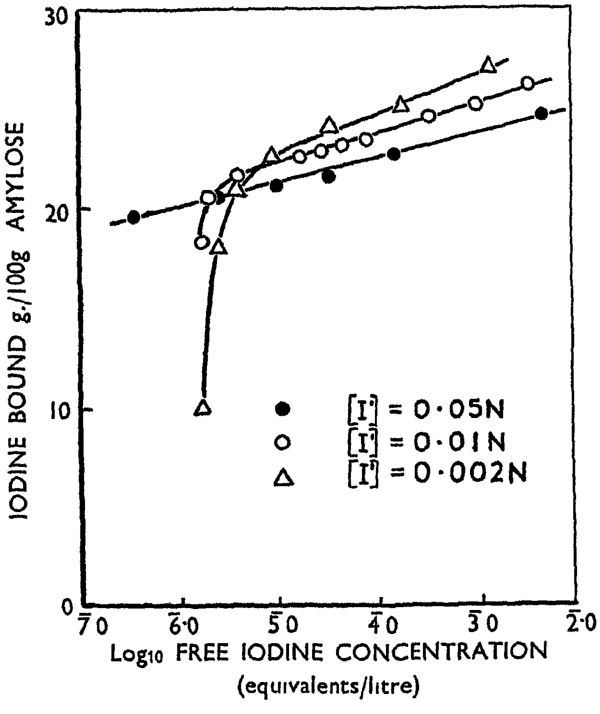

Fig. 2

At each iodide concentration employed, the relation between the amount of iodine bound and the logarithm of the free iodine concentration exhibits a discontinuity when the iodine concentration reaches a certain critical value (Fig. 2), and thereafter becomes linear. The discontinuity is assumed to indicate completion of the first stage of formation of the complex; the concentration of iodine at which it occurs rises as the concentration of iodide is lowered. Further evidence in support of complex formation in two stages has been obtained from spectral absorption data, which will be discussed later. The amount of iodine absorbed by amylose does not reach any limiting value other than that imposed by the solubility of iodine at the concentration of iodide used in the experiment.

It has been suggested[4] that with each amylose chain the first stage of complex formation is completed at a constant iodine activity which is characteristic of the length of the chain, and that the greater the length the lower is the iodine activity required. The sigmoid shape of the portion of the absorption curve which corresponds to this stage has been ascribed to a summation over a range of chain lengths After the first stage of complex formation had been completed any further absorption of iodine was attributed to "adsorption". This rather vague term was presumably intended to imply that the additional iodine does not enter the helices. There are, however, at least two other ways in which the additional iodine might be absorbed, first, according to the helix mechanism by amylose chains or branches with an average length of the same order as the branches in amylopectin, that is, about 20 glucose units; or secondly, by packing into the existing helices. The first possibility may be ruled out, for the number-average D.P. of the potato amylose used in the present experiments was about 900; the amylose could not therefore contain more than 1-2 per cent. by weight of linear, independent chains of the order of 20 glucose units in length. Furthermore, it is most unlikely that the number of non-reducing end groups was more than four times as great as the number of reducing end-groups,* so that not more than 4 per cent by weight of the amylose can be included in branches about 20 glucose units long. About 20 per cent., by weight, of short chains or short branches would be required to account for the increase in the amount of iodine bound by the potato amylose from 20 per cent. at an iodine concentration of 10^{-6}N to 25 per cent. at 10^{-2}N iodine (iodide concentration 0·05N). The second possibility is supported by measurements of the absorption spectra of amylose-iodine complexes.

DETERMINATION OF THE COMPOSITION OF THE COMPLEXES FORMED AT LOW CONCENTRATIONS OF IODIDE

When the iodide concentration was less than 10^{-3}N, the composition of the complexes could not be completely determined. By an indirect method, however, reasonably accurate values for the amounts of iodine bound at 15° C. over a range of iodine concentrations and at iodide concentrations varying from nil to 10^{-3}N have been obtained. Five sets of solutions having a constant concentration of amylose but containing different amounts of iodine and potassium iodide were prepared and adjusted to *pH* 4. All the solutions in any one set had the same total concentration of iodide (10^{-3}N, 10^{-4}N, 10^{-5}N, 10^{-6}N or nil) At the highest concentration of iodide the amounts of iodine bound by the amylose were measured potentiometrically at 15° C. For the range of iodine concentrations employed it was calculated from the results given in the previous section that the amount of iodide absorbed by the amylose was negligible compared with the total amount of iodide present. The optical densities of the solutions were determined at

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* No direct information on the ratio of reducing to non-reducing end groups is available for potato amylose For a sample of sago amylose, the D P (author's measurement) was 840, and the size of the repeating unit (Halsall, Hirst and Jones[14]) was 250±100 Since the intrinsic viscosity of the triacetate of the potato amylose (1 80) was higher than that of the sago amylose triacetate (1·65), it is unlikely that the former was more highly branched than the latter

15° C. by means of a "Spekker" photo-electric absorptiometer with a red filter. The optical densities were corrected for any absorption of light by the free iodine, and the molecular extinction coefficient of the bound iodine in each solution was calculated It was almost constant, increasing slightly when the amount of iodine bound exceeded 24 per cent. of the weight of the amylose The optical densities of the solutions having lower concentrations of iodide were determined and approximate values for the amounts of bound iodine were calculated on the assumption that the molecular extinction coefficient of the bound iodine was constant and independent of the iodide concentration. This assumption may not be quite justifiable but the experiments described in the next section show that the error introduced is only small The concentrations of free iodine were determined by difference, the optical densities corrected for absorption of light by the free iodine, and the amounts of iodine bound recalculated. For a given percentage of iodine absorbed (Fig. 3) the concentration of free iodine increases as the free iodide concentration falls. At the highest iodide concentration (10^{-3}N) the proportion of the iodide bound by the amylose or present as free tri-iodide ions is small; the free iodide concentration is therefore nearly constant and almost equal to the total iodide concentration. The free iodide concentration is not constant at any of the lower concentrations of iodide, but varies with the free iodine concentration and the amount of iodine absorbed by the complex; it cannot be measured accurately but, at a constant concentration of free iodine, the concentration of free iodide will be lower the lower is the total iodide concentration. The complex might not be formed in the absence of added iodide were it not for the formation of iodide ions by hydrolysis of iodine according to the equation $I_2 + H_2O \rightleftharpoons HIO + H' + I'$

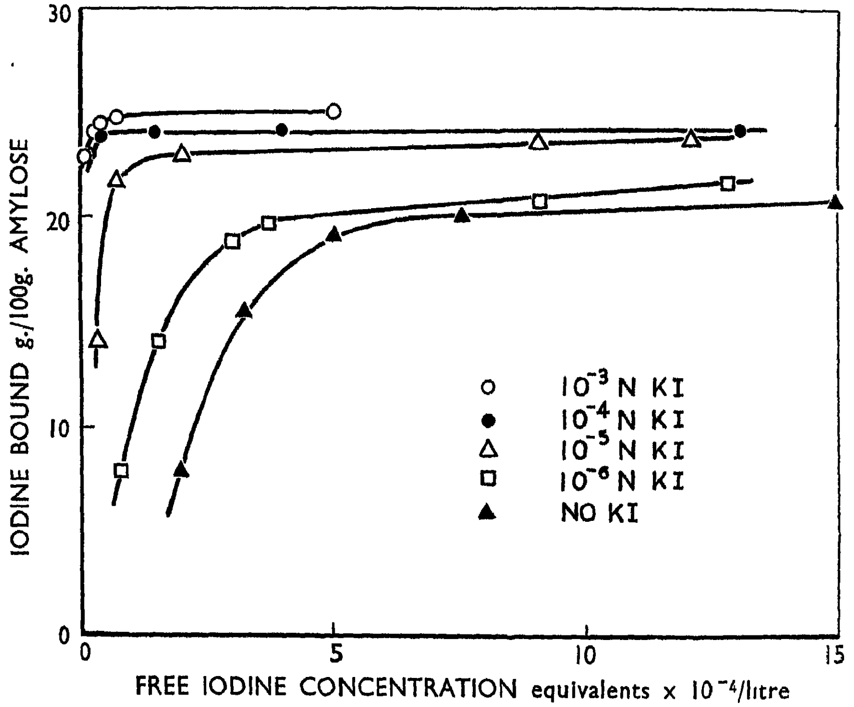

Fig. 3

ABSORPTION SPECTRA OF AMYLOSE-IODINE COMPLEXES

The highest iodide concentration which could be employed without causing precipitation of the complexes at the higher iodine concentrations was 0·005N. With 0·05N iodide, precipitation occurred when only 1 to 2 per cent. of iodine was bound and, with 0·025N iodide, when 5 per cent. of iodine was absorbed.

The absorption spectra of solutions of potato amylose containing from 1 to 24 per cent. of iodine bound in complex formation, and 0·005N in free iodide, are shown in Fig. 4. To secure a strict comparison, the molecular extinction coefficients have been calculated with reference to the actual amounts of iodine bound by the amylose, and the appropriate corrections for any absorption of light by free iodine have been applied. The maximum extinction coefficients of all the complexes are substantially equal in magnitude. When less than 21·0 per cent. of iodine is bound, that is, during the first stage of complex formation, the complexes have identical absorption spectra, but when more than 21·0 per cent. of iodine has been absorbed, the absorption spectrum moves progressively in the direction of higher wavelengths. Thus, the absorption maximum was at 6250 Å when 21·0 per cent. of iodine was absorbed, and at 6600 Å when 24·0 per cent. was absorbed.

Baldwin, Bear and Rundle[5] have shown that the maximum extinction coefficients of amylose-iodine complexes of given iodine content (12·5 g. iodine/100 g. amylose) occur at a higher wavelength, the higher is the average molecular weight of the amylose. Hence, if the longer chains absorb iodine at lower free iodine activities than the shorter chains, the maximum extinction coefficient might be expected to move to a shorter wavelength as the iodine absorption increases from 1 to 21 per cent. Preliminary fractionation data suggest, however, that less than 10 per cent. of the amylose used in the experiments had a chain length more than 50 per cent. in excess of the mean value, and measurements of the absorption spectra of iodine complexes of amylose differing in average chain length (Table II) have indicated that there is a shift of only 100 Å in the wavelength of maximum absorption when the chain length changes from 950 to 300, that is, the wavelength of maximum absorption diminishes by about 25 Å for a 50 per cent.

Table II

Material	Number average D P.	Maximum extinction coefficient of iodine complex	
		Magnitude	Wavelength (Å)
Author's data			
Pure sago amylose	950	$3{\cdot}82 \times 10^4$	6250*
Pure maize amylose	550	$3{\cdot}80 \times 10^4$	6200*
Pure maize amylose, slightly degraded during separation	310	$3{\cdot}70 \times 10^4$	6150*
Pure maize "crystalline" amylose	300	$3{\cdot}72 \times 10^4$	6150*
Pure potato amylose	940	$3{\cdot}85 \times 10^4$	6250*
Data of Baldwin, Bear and Rundle[5]	D P (from osmotic pressure and viscosity data)		
Impure potato amylose	500	—	6280†
Impure maize amylose	250	—	6180†
Impure maize "crystalline" amylose	175	—	6050†

* Iodine complexes contained 15% bound iodine, iodide concentration 0·005N

† Iodine complexes contained about 14% bound iodine, iodide concentration 0·005N.

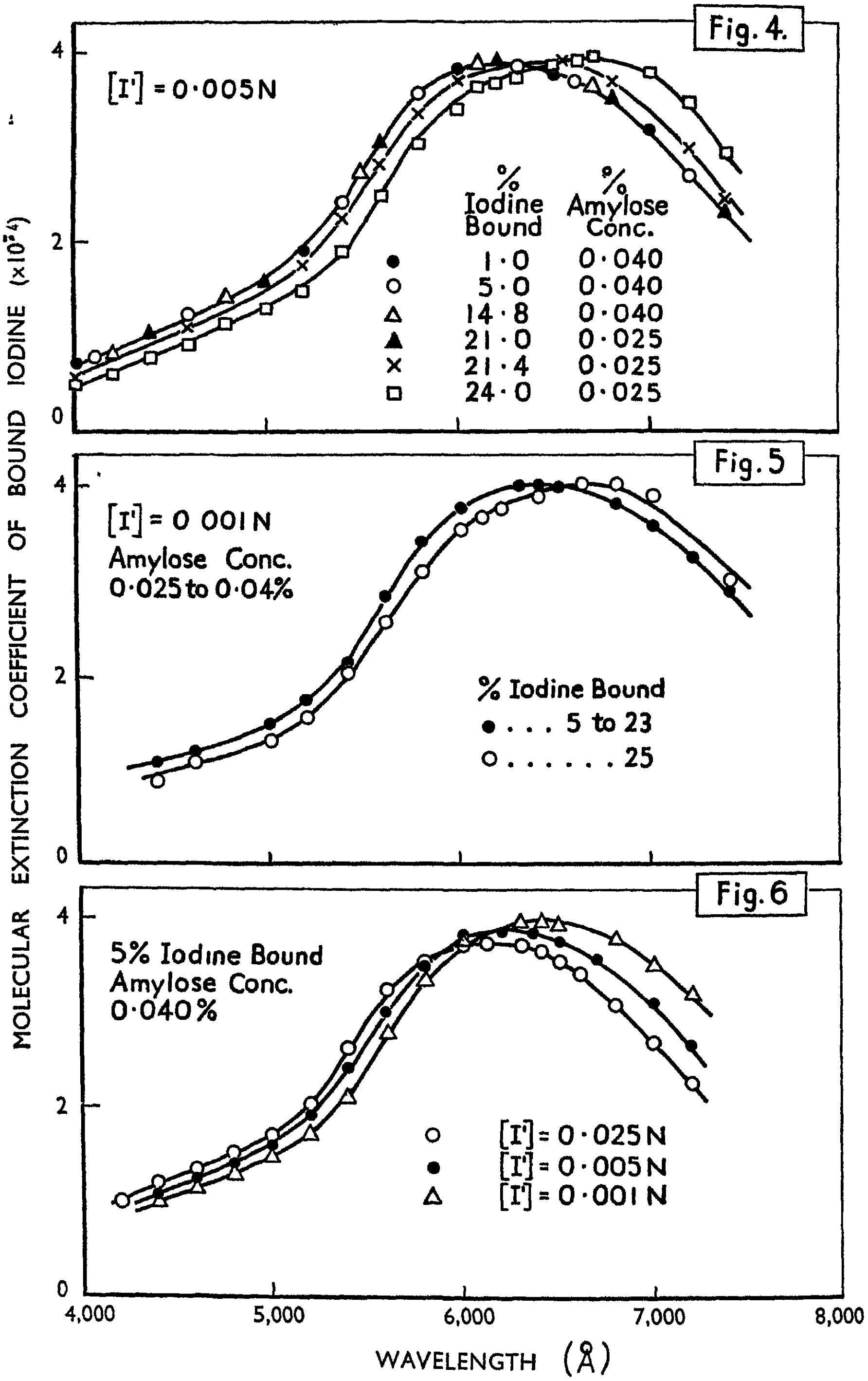
Fig. 4.
[I'] = 0·005N
% Iodine Bound
% Amylose Conc.
● 1·0 0·040
○ 5·0 0·040
△ 14·8 0·040
▲ 21·0 0·025
× 21·4 0·025
□ 24·0 0·025
Fig. 5
[I'] = 0 001 N
Amylose Conc. 0·025 to 0·04%
% Iodine Bound
● . . . 5 to 23
○ 25
Fig. 6
5% Iodine Bound
Amylose Conc. 0·040%
○ [I'] = 0·025 N
● [I'] = 0·005 N
△ [I'] = 0·001 N
MOLECULAR EXTINCTION COEFFICIENT OF BOUND IODINE (×10⁻⁴)
0
2
4
4,000
5,000
6,000
7,000
8,000
WAVELENGTH (Å)

change in chain length within this range. Hence the wavelength of maximum absorption when 2 per cent. of iodine is bound cannot differ by more than 25 Å from that when 21·0 per cent. of iodine is bound, and this change is within the limits of the experimental error.

The increase in the wavelength of maximum absorption when the amount of iodine absorbed exceeds 21·0 per cent. suggests that after the first stage of complex formation has been completed, additional iodine is taken into iodine-filled helices. By increasing the number of iodine molecules in the resonating complex, and also decreasing the intermolecular spacing this would greatly influence the resonance energy, which is a very sensitive function of the distance between the iodine molecules[3] and hence would produce a change in the wavelength of maximum absorption

The relation between the wavelengths of maximum absorption of amylose-iodine complexes and the degrees of polymerisation of the amyloses observed in the present experiments is not in agreement with that found by Baldwin, Bear and Rundle (included in Table II for comparison), although the amylose complexes contained approximately the same amount of bound iodine and were prepared in the presence of the same concentrations of iodide. The amylopectin present in the samples employed by Baldwin, Bear and Rundle would not affect the wavelength of maximum absorption, for it would not absorb an appreciable amount of iodine under the conditions used. The most probable explanation of the discrepancy is that the values given by Baldwin for the degrees of polymerisation of the amylose samples are much too low. The recently published results of Potter and Hassid[17] confirm this view. These workers report values for the number-average degree of polymerisation of the amyloses of several starches which are in fair agreement with those given in the present paper, but are approximately twice as large as the corresponding values given by Baldwin. Thus, though the molecular weights of the potato and maize amyloses used in the present experiments are about twice as great as those of the samples used by Baldwin, Bear and Rundle, the wavelengths of maximum absorption for the iodine complexes are very nearly the same.

The absorption spectra of amylose-iodine complexes vary with the free iodide concentration. This might be expected since the proportion of iodide ions in the complex must have a profound influence upon the molecular interactions. The spectral absorption curves for potato amylose-iodine complexes (1 to 25 per cent. iodine bound) at an iodide concentration of 0·001N (Fig. 5) are generally similar to those at an iodide concentration of 0·005N, except that the wavelength of maximum absorption does not increase until a higher iodine content (23·5 per cent.) is reached, in agreement with the observation that the first stage of complex formation is not completed until at least this amount of iodine has been absorbed (compare Curve 3, Fig 3, for 0·002N iodide). The curves for three iodide concentrations (0·025N, 0 005N and 0·001N) and a constant iodine absorption (5 per cent) (Fig. 6) indicate that the maximum extinction coefficient increases slightly in magnitude and occurs at a higher wavelength as the iodide concentration decreases.

EXPERIMENTAL

Materials

The preparation of the pure samples of amylose has been described elsewhere.[12] "Crystalline Maize Amylose"[13] was recrystallised twice from very dilute (0·1 per cent.) solution in water saturated with butanol; the iodine absorption[10] of the final product was 21·0 per cent. The number-average molecular weights of the various materials were calculated from the osmotic pressures of solutions of their triacetates in chloroform; details will be given in a subsequent publication. Some properties of the amyloses are summarised in Table III.

Table III

Material	Iodine absorption (g /100 g amylose)	Intrinsic viscosity of triacetate in nitroethane (concentration expressed as g. solute per 100 ml solution)	D P (Number average)
Potato amylose . . .	21·0	1·80	940
Maize amylose .. .	20·8	1·11	550
Maize amylose, accidentally degraded during extraction .	21·0	0·62	310
Sago amylose .	21·0	1·84	950
Crystalline maize amylose .	21 0	0·55	300

Preparation of Solutions for Analysis

Amylose, in the form of the butanol complex, was dissolved in hot water saturated with butanol, and the butanol was removed by evaporation; the water lost was replaced continuously. The concentration of all amylose solutions was determined by the wet-combustion of a sample with potassium dichromate and sulphuric acid,[15,16] a correction being applied to allow for the slightly low values (98 per cent. of theoretical) given by this method. To the requisite amount of amylose solution, known amounts of iodine and potassium iodide were added, and the solution was diluted to a definite volume. All solutions were adjusted to a *pH* value of 4 with very dilute sulphuric acid.

Determination of the Activity of Molecular Iodine

180 ml. of a control or test solution was placed in one limb (A) of a Jones and Kaplan equilibrator[11] and 180 ml. of acidified water was placed in the other limb (B). Equilibrium was established by rocking the apparatus for 20 hours in a thermostat maintained at 25·0° C. The activity of molecular iodine (I_2) was then equal in both limbs, and was determined by titrating a 50 ml. portion of the solution from (B) with standard thiosulphate solution; amylose was used as the indicator, and, to ensure a sharp end point, sufficient potassium iodide (about 0·05 g) was added immediately before titration The total iodine in the control or test solution was determined after equilibration, by titrating with thiosulphate. If the iodine complex had precipitated it was necessary to add a slight excess of thiosulphate and then titrate back with standard iodine solution; in a direct titration a good end point was not obtained

Potentiometric Titration

A portion of the test solution (taken from the equilibrator when $(I_2)_t$ had been determined) was placed in one cell of the differential titration apparatus The cell (Fig. 7) was so designed that it could be filled completely with solution, and volatilisation of iodine was thereby prevented. In the other cell (which was identical with those employed previously[10]) a known volume of a solution of potassium iodide, adjusted to *pH* 4, and having nearly the same concentration as the free iodide in the test solution, was placed. A pilot experiment was carried out, if necessary, to determine the concentration required. The apparatus was placed in a thermostat at 25·0° C, with the stirrers running, until both solutions had reached the thermostat temperature. Iodine solution having the same concentration in free iodide as the control

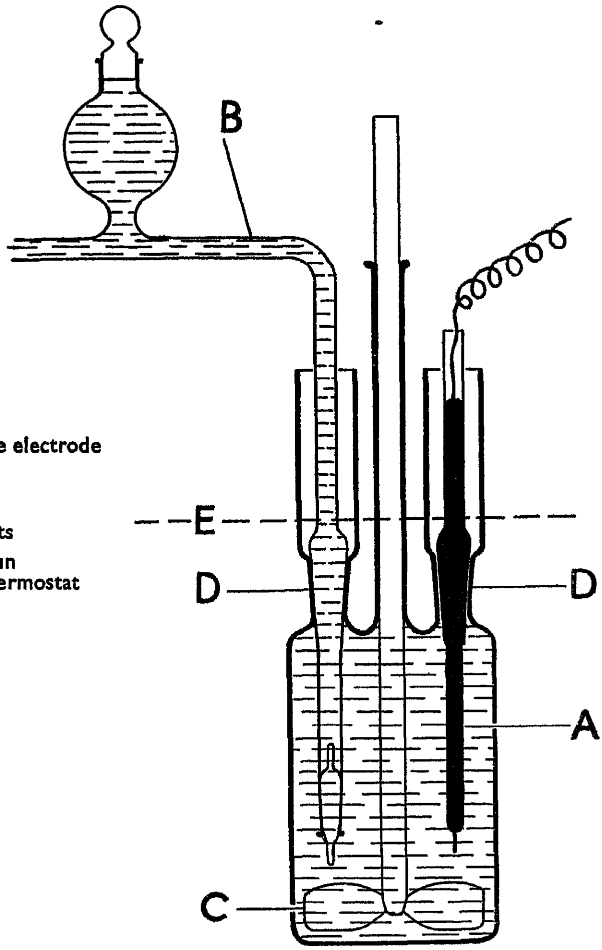

Fig. 7

A=Platinum wire electrode
B=KCl bridge
C=Glass stirrer
D=Ground joints
E=Water level in thermostat

solution was added to it until there was no P D between the electrodes. Wherever there was any danger of volatilisation of an appreciable amount of iodine from the control solution during the titration, its final iodine concentration was determined by titration with standard thiosulphate.

Spectrophotometry

To measured amounts (20-40 ml.) of a 0·1 per cent. solution of amylose, the calculated quantities of solutions of iodine and potassium iodide, respectively, were added to give the desired iodine absorptions and free iodide concentrations, and the solutions were diluted to 100 ml. After equilibrium had been reached, the absorption spectrum of each solution was measured at room temperature (16-19° C.) by means of a photo-electric spectrophotometer, over the range 4000-6800 A in a cell of such a thickness (0·05-1·00 cm.) that the optical density at maximum absorption lay between 0·4 and

0·8. For each solution an appropriate control having the same concentrations in free iodine and free iodide was used. The free iodine concentration and hence the amount of iodine bound was determined in each case by potentiometric titration at the temperature at which the absorption spectrum was measured.

Much of the experimental work has been carried out by Miss M. M. Bridges.

REFERENCES

[1] Rundle and Edwards *J Amer. Chem Soc* , 1943, 65, 2200
[2] Rundle and French *J Amer. Chem. Soc.*, 1943, 65, 558, 1707.
[3] Stein and Rundle *J. Chem Phys* , 1948, 16, 195.
[4] Bates, French and Rundle. *J. Amer Chem. Soc* , 1943, 65, 143.
[5] Baldwin, Bear and Rundle. *J. Amer Chem Soc.*, 1944, 66, 111.
[6] Rundle and Baldwin. *J. Amer Chem Soc* , 1943, 65, 554
[7] Foster *Iowa State Coll. J. of Sci* , 1943, 18, 36
[8] Baldwin *Iowa State Coll J of Sci.*, 1943, 18, 10
[9] Gilbert and Marriott *Trans Faraday Soc.*, 1948, 44, 84
[10] Higginbotham and Morrison *Shirley Inst Mem.*, 1948, 22, 141, and *J. Textile Inst.*, 949, 40, T201.
[11] Jones and Kaplan *J. Amer Chem Soc.*, 1928, 50, 1600.
[12] Higginbotham and Morrison *Shirley Inst. Mem* , 1948, 22, 148, and *J Textile Inst.*, 1949, 40, T208.
[13] Kerr and Severson *J. Amer Chem. Soc* , 1943, 65, 193.
[14] Halsall, Hirst and Jones. *J Chem. Soc.*, 1948, 27
[15] Birtwell and Ridge. *Shirley Inst. Mem.*, 1928, 7, 37, and *J. Textile Inst* , 1928, 19, T341.
[16] Richardson, Higginbotham and Fairow. *Shirley Inst. Mem* , 1935, 14, 63, and *J. Textile Inst* , 1936, 27, T131.
[17] Potter and Hassid. *J. Amer. Chem Soc.*, 1948, 70, 3774.

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49—THE FRACTIONATION OF STARCH
Part IV—THE AMYLOPECTIN-IODINE REACTION

By R. S. Higginbotham

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The composition and absorption spectra of amylopectin-iodine complexes and glycogen-iodine complexes have been determined for a wide range of iodine concentrations. Provided that the concentration of free iodine is sufficiently high, the amylopectins absorb as much iodine as amyloses do. It is inferred, therefore, that amylopectins absorb iodine partly by a helix mechanism involving chains of iodine molecules and tri-iodide ions, and partly by adsorption of single iodine molecules or single tri-iodide ions. Spectrophotometric data support this view. The proportion of iodine bound by the helix mechanism varies with the total amount of iodine absorbed and with the identity of the amylopectin. These variations may be related to the distributions of branch lengths in the amylopectins.

The amylopectins are highly branched polysaccharides. The repeating unit contains, on an average, from 18 to 24 glucose units,[1,2] its size varying to some extent with the botanical variety of the parent starch. Haworth[3,4] has postulated a stepwise arrangement of branches but the more random arrangement of Meyer[2] would seem to be in better accord with the experimental evidence. The maximum yield of maltose which can be obtained by the action of β-amylase upon amylopectin is about 55 per cent. of the theoretical value,[5,6] suggesting that external branches comprise a little more than half the molecule The distribution of the lengths of the branches, which has not yet been determined, probably has an important influence upon the physical behaviour of the amylopectins.

The amyloses take up iodine in two stages.[7,8] Depending on the iodide concentration, from 19 to 24 per cent of iodine is taken up at a very low and nearly constant iodine activity; thereafter a large increase in the free-iodine activity causes only a small change in the amount of iodine bound. In the first stage of complex formation the iodine activity corresponding to the absorption of a given amount of iodine at a given iodide concentration is a function of the average molecular chain-length of the amylose.[9] From this it has been deduced that when iodine is added to a solution of amylose the longer chains react with iodine before the shorter ones. Since the amylopectins consist of short amylose chains linked together, their iodine absorption curves should be related to the distributions of branch-lengths, the longer branches absorbing iodine at the lower free iodine activities, and progressively shorter branches reacting as the free-iodine activity increases. The absorption spectra of amylopectin-iodine complexes in equilibrium with different concentrations of free iodine should afford similar information, for the wavelength of maximum absorption of iodine complexes of amylose or degraded amylose is dependent on molecular chain-length, and decreases from 6250 Å at a chain length of 800 glucose units[8] to 5000 Å at a chain length of 7 glucose units.[10]

Amylopectins from different varieties of starch do not display identical affinities for iodine,[7] nor are the absorption spectra of their iodine complexes identical,[11] and it has been suggested that these differences are related to differences in the sizes of the repeating units of the amylopectins. The results are not convincing. The iodometric measurements and the determinations of the sizes of the repeating units have been made with different samples of amylopectin by different workers who have applied no adequate corrections for the effects of the small amounts of amylose present in all the samples. In the potentiometric measurements the range of concentrations of free iodine was such that the amount of iodine absorbed by amylopectin was never more than 5 per cent. and in the spectrophotometric work it was generally much less.

The object of the present investigation has been to examine iodine complexes of amylopectins and glycogen formed over a wide range of iodine concentrations in order to obtain a more complete picture of the manner in which the iodine is absorbed; it was hoped, also, to obtain some indication of the distributions of the lengths of the branches in the materials.

DETERMINATION OF THE COMPOSITION OF THE COMPLEXES

The amounts of iodine absorbed by sago, tapioca, potato, maize and waxy maize amylopectins, and by glycogen, have been measured at concentrations of free iodine ranging from 10^{-6}N to 10^{-1}N. The effect of varying the iodide concentration over the range 0·01 to 0·5N has been examined, and the ratio of the amounts of iodine to iodide absorbed has been determined wherever possible. The experimental methods were those used to investigate the reaction between amylose and iodine.[8] The spectral absorption curves of amylopectin-iodine complexes containing various amounts of bound iodine within the range 3 per cent. to 22 per cent. have also been measured.

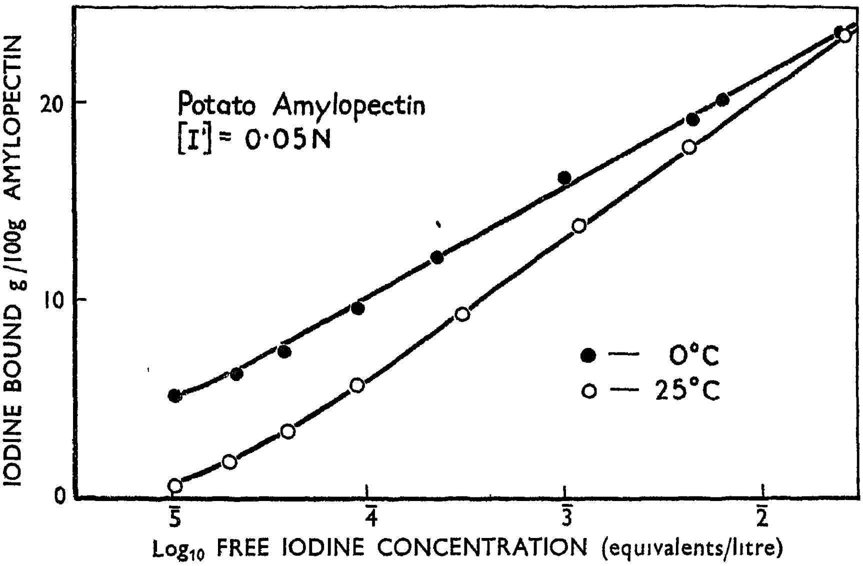


Fig. 1

All the amylopectins contained small amounts of amylose (Table VI) which have been determined in order to correct the results for any absorption of iodine by this impurity.

When the amount of iodine absorbed by an amylopectin exceeds 5 per cent. (5 g./100 g. of amylopectin) it is related linearly to the logarithm of the free iodine concentration. At any given iodine concentration, the percentage of iodine bound increases as the temperature falls, the effect of temperature being most marked when the free iodine concentration is low. These findings are illustrated by the iodine absorption curves for potato amylopectin at a free iodide concentration of 0·05N (Figs. 1 and 2).

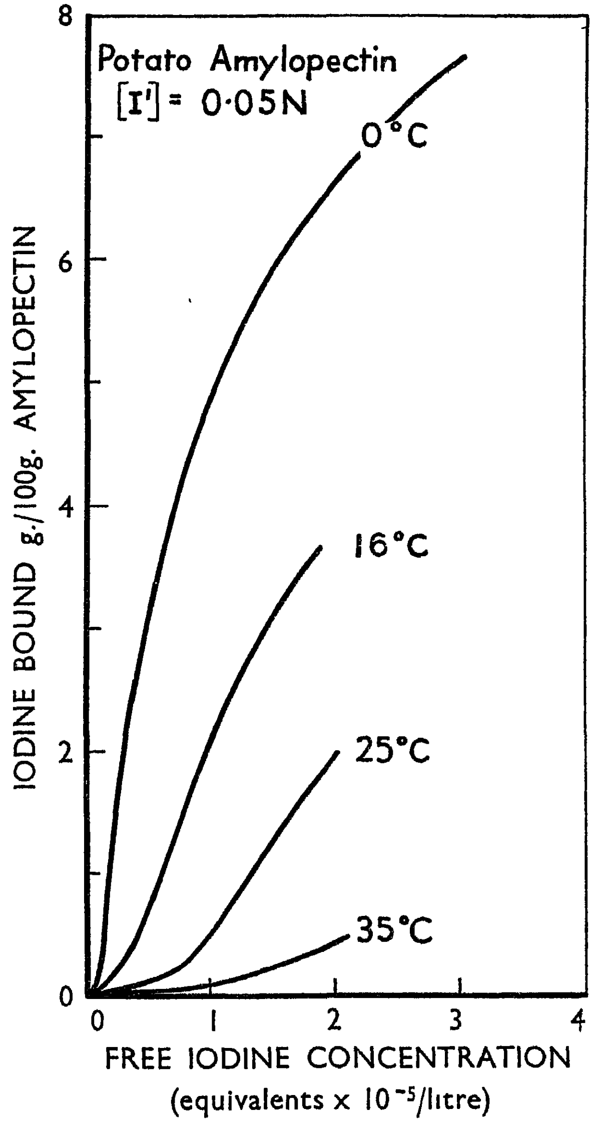


Fig. 2

The percentage of iodine absorbed by potato amylopectin at any free iodine concentration above 10^{-5}N is independent of variations in the free iodide concentration over the range 0·01N-0·5N (Fig. 3). Furthermore, in the region where measurements were practicable, the ratio $C_{I'}$ (equivalents iodide bound)/C_I (equivalents iodine bound) is nearly independent of the iodide concentration, though it varies slightly with the amount of iodine bound (Table I). This behaviour is very different from that of amylose,[8] with which both $C_{I'}/C_I$ and the amount of iodine absorbed are dependent upon the iodide concentration Thus, at iodide concentrations of 0·05N and 0·01N the values of $C_{I'}/C_I$ were 0 81 and 0 47, respectively. These differences suggest that the mechanisms by which amylose and amylopectin absorb iodine must differ; further evidence for this view will be presented later (see p. 802).

Table I

Amylopectin concentration g./100 ml.	[I′]	(I$_2$)	Concentration total free iodine	g. iodine bound/100 g amylopectin	$\frac{C_{I'}*}{C_I}$
	equivalents/litre				
2·920	0·508	0·000332	0·132	28·5±·2	0·25±·04
1·160	0·500	0·000076	0·0274	22·8±·2	0·32±·10
1·175	0·0506	0·000743	0·0275	23·5±·2	0·28±·02
1·175	0·0470	0·000123	0·00435	17·7±·1	0·34±·05
0·457	0·0102	0·000190	0·00159	14·5±·1	0·32±·01

*Equivalents iodide bound by amylopectin/Equivalents iodine bound by amylopectin.

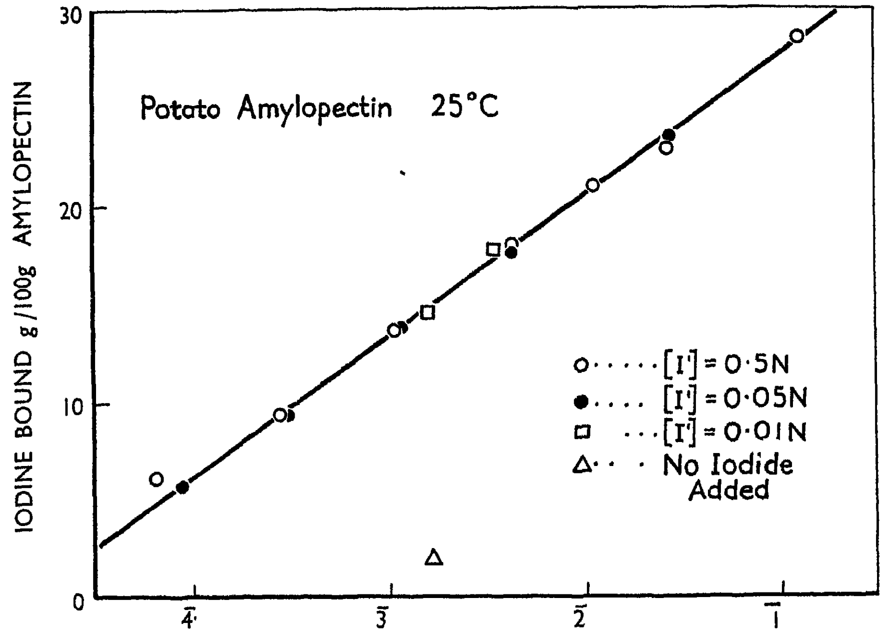


Fig. 3

When the iodide concentration exceeds 0·15N and not less than 23 per cent of iodine is bound, the amylopectin-iodine complex is partially or completely precipitated, but otherwise no precipitation occurs. The amount of iodine absorbed at a given concentration of free iodine when no iodide is added is very much less than when iodide is present (Fig. 3). Thus, at a free iodine concentration of 0·0016N, 14·5 per cent. of iodine was absorbed when the iodide concentration was 0·01N, but only 1·8 per cent. when the only iodide ions were derived from the hydrolysis of iodine.

The iodine absorption curves for the different amylopectins and glycogen, at an iodide concentration of 0·05N and a temperature of 25° C., are shown in Figs. 4 and 5. The curves for sago and maize amylopectins are identical. Tapioca amylopectin absorbs slightly more iodine when the concentration of free iodine is below 3×10^{-4}N, but at higher iodine concentrations it behaves identically with maize and sago amylopectins. At all iodine concentrations waxy maize amylopectin absorbs slightly less and potato amylopectin considerably more iodine than sago and maize amylopectins. There is a suggestion (Table II), that for a given absorption of iodine, maize, sago and tapioca amylopectins bind a slightly higher proportion of iodide than potato amylopectin.

Glycogen binds considerably less iodine than any of the amylopectins, the difference being most marked at a low concentration of iodine.

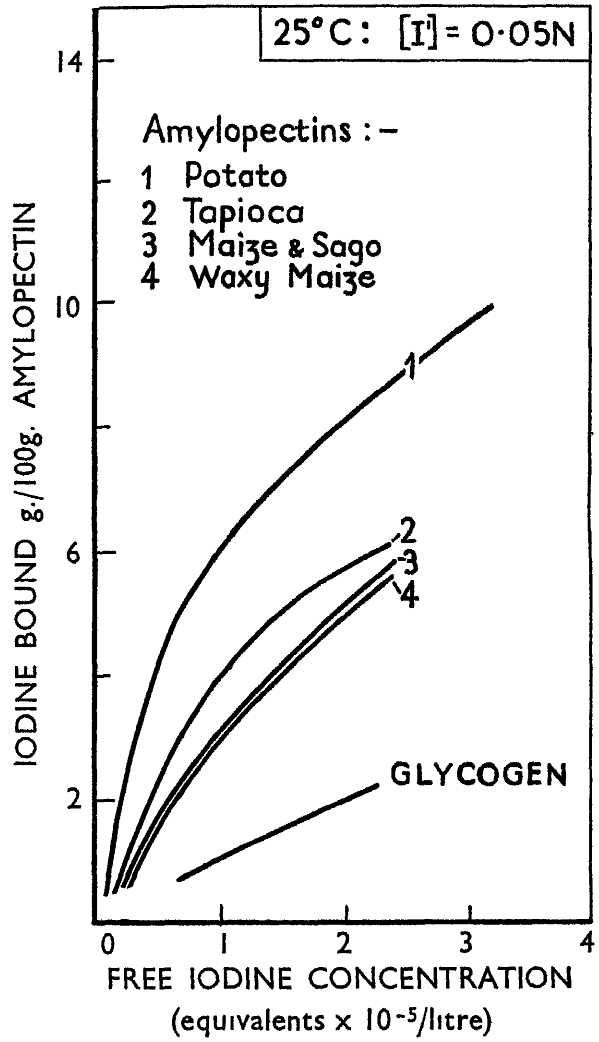


Fig. 4

Table II

Amylopectin	Amylopectin concentration g /100 ml	[I']	(I$_2$)	Concentration total free iodine	g iodine bound/100 g. amylopectin	$\frac{C_{I'}}{C_I}$
		Equivalents/litre				
Potato . .	1·175	0·0506	0·000743	0·0276	23·5	0·28 ± ·02
Tapioca . .	1·187	0·0493	0·000674	0·0265	22·5	0·34 ± ·02
Maize . .	1·170	0·0491	0·000678	0·0265	22·2	0·38 ± ·02
Sago .	1·195	0·0494	0·000679	0·0267	22·0	0·35 ± ·02

If only the outside branches in amylopectin or glycogen can absorb iodine by helix formation and allowance is made for steric hindrance at the branch points, the percentage of iodine bound in this way cannot exceed half of that bound by amylose under the same conditions. At low iodine concentrations it will be very much smaller because of the short average length of the branches. At high concentrations of free iodine, however, the amylopectins bind as much iodine as the amyloses, and as the only limit appears to be that imposed by the solubility of iodine, the helix mechanism cannot be the only means of absorption. The proportion and average size of the branches capable of helix formation cannot therefore be deduced from the absorption data alone, though it is perhaps justifiable to conclude that the free branches of potato amylopectin may have a higher average length than those of the other amylopectins.

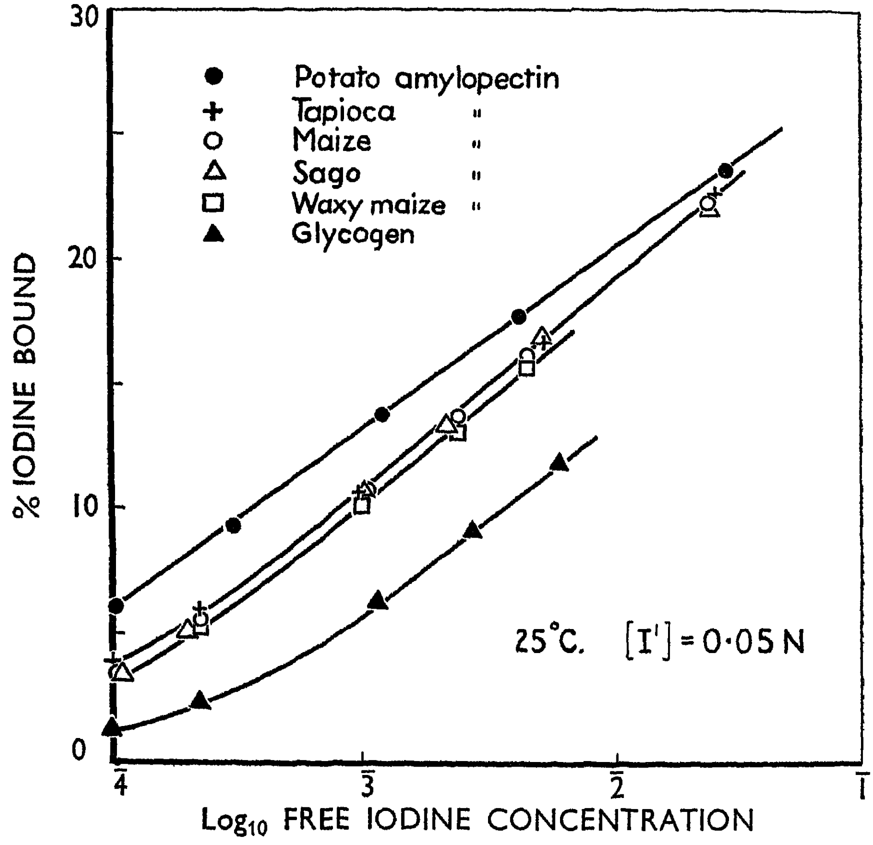


Fig. 5

ABSORPTION SPECTRA OF THE COMPLEXES

The mechanism of the reaction between iodine and amylopectin has been clarified to some extent by a study of the absorption spectra of amylopectin-iodine complexes. All measurements were carried out at room temperature (18-20° C) and at a constant concentration (0·05N) of free iodide. To enable the spectra of complexes containing different amounts of bound iodine to be compared, all molecular extinction coefficients have been calculated with reference to the bound iodine. Corrections have been applied for absorption of light by the free iodine and by the iodine complex of any amylose present. The importance of the latter correction may be illustrated by the data (Fig. 6)

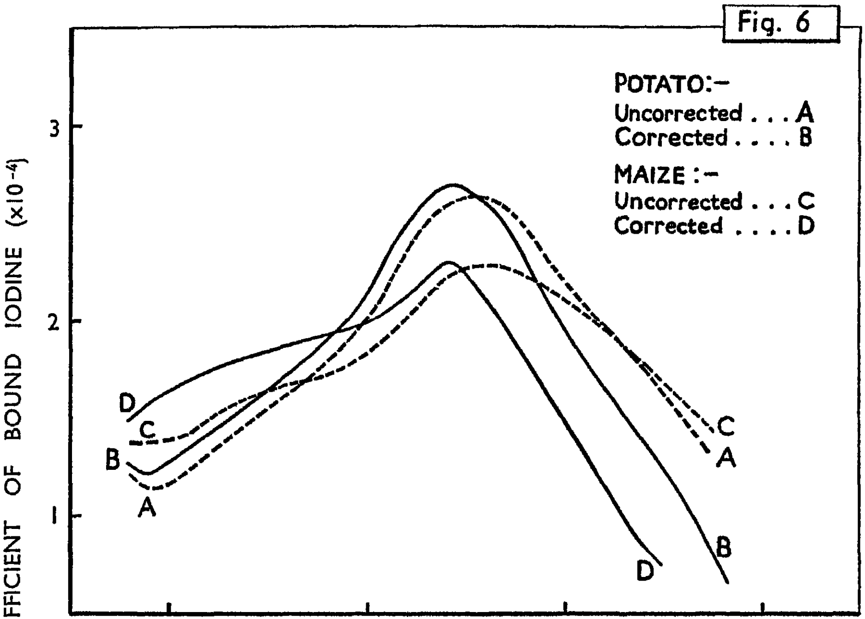


Fig. 6

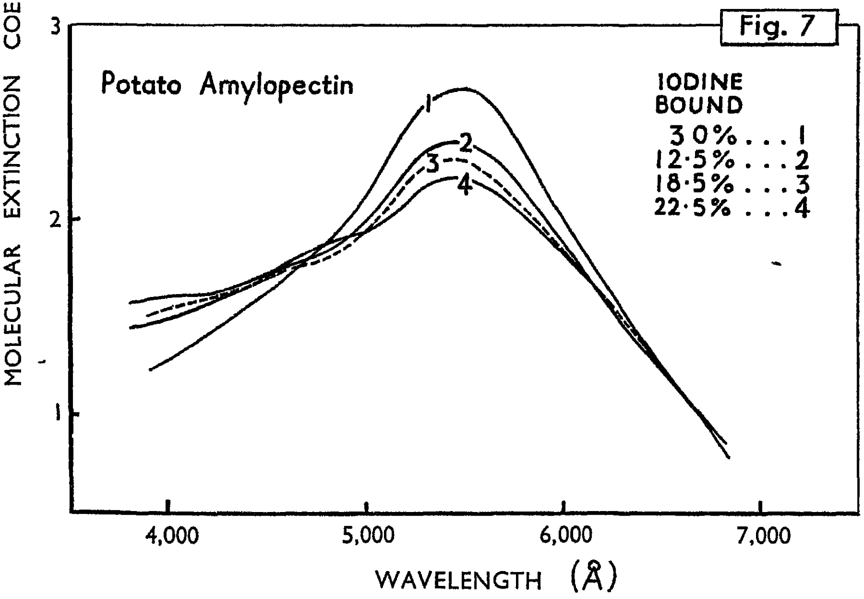


Fig. 7

for potato amylopectin containing 2 per cent. of amylose, and maize amylopectin containing 6·3 per cent of amylose, 3 per cent. of iodine being bound by the amylopectin fraction in each case Without correction, the maximum extinction coefficient for potato amylopectin appears to be at 5500 Å and that for maize amylopectin at 5650 Å, but when corrections are applied for the contributions of the amylose-iodine complexes the maximum is at 5400 Å for both. The molecular extinction coefficients may be in error by as much as 100 per cent. at the higher wavelengths unless allowance is made for the influence of the amylose present. As the percentages of iodine bound by the amylopectin increases, the effect of the amylose is proportionately less since it becomes almost saturated with iodine when the amount of iodine absorbed by the amylopectin is still very small, about 1 per cent.

The influence of the iodine content upon the absorption spectrum may be illustrated by the results (Fig. 7) for potato amylopectin-iodine complexes containing up to 22·5 per cent. of bound iodine As the percentage of iodine

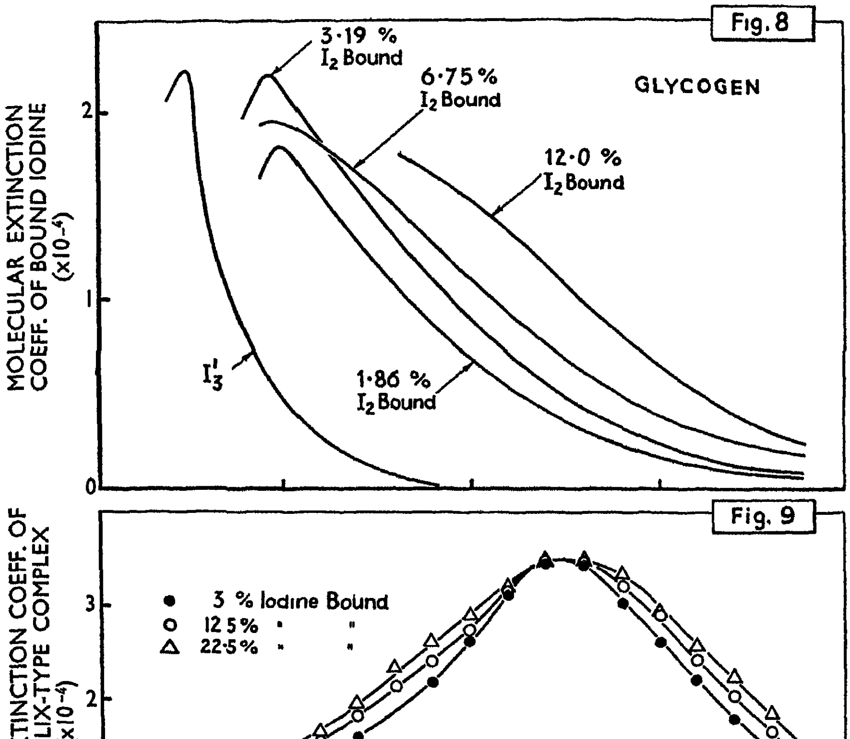


Fig. 8

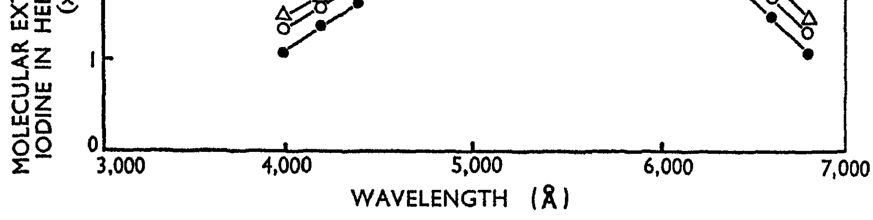


Fig. 9

bound increases, the maximum extinction coefficient diminishes, but the wavelength at which it occurs remains constant; moreover, the extinction coefficients increase between 3800 Å and 4200 Å, and decrease between 5000 Å and 6000 Å. From this behaviour it seems that two types of complex may be present with absorption maxima at about 5400Å and at or below 4000 Å, and that their relative proportions vary with the amount of iodine bound. The complex with an absorption maximum near 5400 Å may well be of the amylose or "Helix" type and be derived from outside branches of the polysaccharide with an average length of rather less than

20 glucose units, for Swanson[10] has observed that the iodine complex of a degraded amylose with an average chain length of 14 to 18 glucose units exhibited an absorption maximum of 5400 Å. In the other complex, iodine is probably bound by simple adsorption of tri-iodide ions or iodine molecules, the results of spectrophotometric measurements upon glycogen-iodine complexes support this view.

With glycogen, as with amylopectin, the absorption spectrum changes with the amount of iodine bound but the wavelength (4000 Å) of maximum absorption does not (Fig. 8). As the amount of iodine absorbed increases the extinction coefficients at higher wavelengths increase. Branches less than six glucose units long presumably cannot absorb iodine by a helix mechanism since they cannot form a complete helix turn. The lower limit for the wavelength of maximum absorption of a helix-type complex is therefore about 5000 Å[10] and the maximum at 4000 Å cannot correspond to iodine bound by helix formation. Since the maximum extinction coefficient for tri-iodide ions occurs at 3500 Å, and has almost the same magnitude as that for the glycogen-iodine complexes, it seems probable that glycogen binds iodine mainly by adsorption of single tri-iodide ions. The progressive change in the spectrum as the amount of iodine absorbed increases may arise from an increasing proportion of helix-type complexes formed from external branches with an average length of about 12 glucose units These would have absorption maxima in the region 5000-5200 Å, and would only be stable at very high concentrations of free iodine. The absorption spectra of potato-amylopectin iodine complexes have been analysed on the assumption that two components are present. To do so, it has been necessary to assume first that the maximum molecular extinction coefficient of the helix component is constant at $3{\cdot}5\times10^4$, and secondly, that glycogen binds iodine solely by adsorption so long as the amount does not exceed 1·8 per cent. The value for the maximum molecular extinction coefficient of the helix component is regarded as a very rough approximation only; it seemed reasonable to assume that it would be slightly lower than the values found for amylose-iodine complexes (about $3{\cdot}7\times10^4$) but considerably higher than the highest value found for an amylopectin-iodine complex ($2{\cdot}7\times10^4$). Let

ϵ_1 = the maximum molecular extinction coefficient of the whole complex

ϵ_2 = the maximum molecular extinction coefficient of the helix component

ϵ_3 = the molecular extinction coefficient of the adsorption component at the wavelength of maximum absorption of the whole complex (taken from the absorption spectrum of a glycogen-iodine complex containing 1·8 per cent. bound iodine) $=0{\cdot}4\times10^4$

$$\left.\begin{array}{l}\epsilon_{n1}\\ \epsilon_{n2}\\ \epsilon_{n3}\end{array}\right\}=\left\{\begin{array}{l}\text{the molecular extinction coefficients of the whole complex, the}\\ \text{helix component and the adsorption component, respectively, at}\\ \text{any given wavelength, } n.\end{array}\right.$$

x = the percentage of the total iodine in the complex which is bound by adsorption.

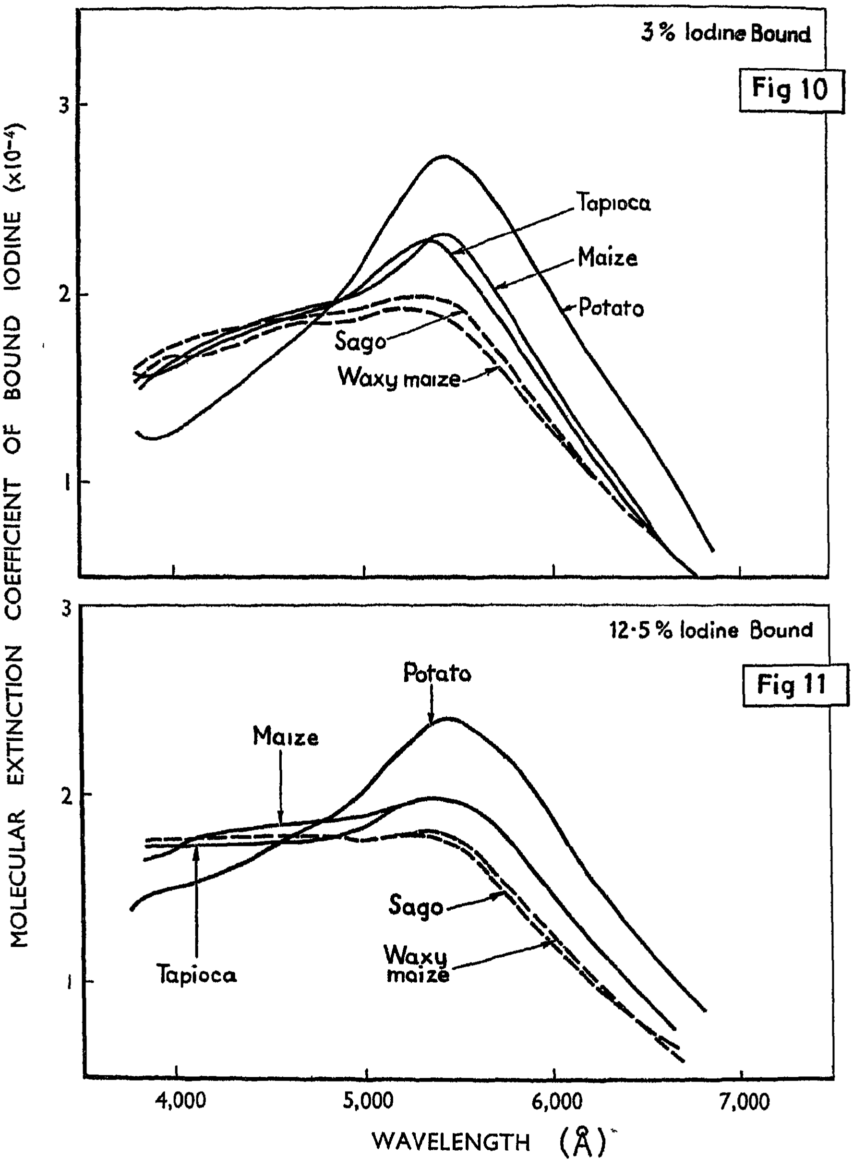
Then
$$x=\frac{100\,(\varepsilon_2-\varepsilon_1)}{\varepsilon_2-\varepsilon_3} \qquad \ldots \qquad (1)$$

and
$$\frac{(100\cdot\varepsilon_{n1}-x\cdot\varepsilon_{n3})}{100-x}=\varepsilon_{n2} \qquad \ldots\ldots \qquad (2)$$

Hence the complete absorption spectrum of the helix component can be calculated.

The absorption spectra of the helix-components of potato amylopectin-iodine complexes containing 3 per cent., 12·5 per cent. and 22·5 per cent.

of bound iodine are plotted in Fig. 9, the values of x being, respectively, 26 per cent., 36 per cent. and 42 per cent. Though they have no absolute quantitative significance, they clearly indicate that the proportion of iodine bound by adsorption rises as the total amount of iodine bound increases.



Moreover, the value of x is about 40 per cent. in the range where amylopectin binds approximately the same amount (24 per cent.) of iodine as amylose, and it has been deduced (p 800) that amylopectin cannot bind more than half as much iodine by helix formation as amylose. The three curves are not identical, some broadening occurs as the amount of bound iodine increases, though the position of the maximum is nearly constant. The increase in the absorption of light at lower wavelengths as the amount of iodine bound increases may arise from the presence of very short external branches resembling those in glycogen which are able to form stable helix-type complexes at high concentrations of iodine. The wavelength of maximum absorption for amylose-iodine complexes rises when the concentration of free iodine is increased beyond a certain minimum value;[8] similar behaviour with the iodine complexes of the longer branches in amylopectin would account for the increase in absorption at higher wavelengths with increase in the amount of bound iodine. If the two effects neutralise one another in the middle part of the absorption curve, the wavelength of maximum absorption will be constant.

It is probable that the adsorbed iodine will be attached to portions of the amylopectin molecules which are unable to form complete helices, but which can take up such a configuration that they have a resultant dipole moment and can therefore induce polarisation in iodine molecules or tri-iodide ions The inner portions of the molecule, and possibly external branches less than six glucose units in length, might well behave in this way

The ratio of iodide to iodine in the amylopectin-iodine complex is about o 3. If half the total iodine is adsorbed in the form of tri-iodide ions, the ratio of iodide to iodine ($C_{\text{I}'}/C_{\text{I}}$) in the helix component will be $[(100\times 0\cdot 3)-(50\times 0\cdot 5)]\div 50=0\cdot 1$ whereas for the corresponding amylose-iodine complex (iodide concentration–0·05N) it is o 8. On the other hand, if molecular iodine is adsorbed, the ratio in the helix complex would be $[(100\times 0\cdot 3)-(50\times 0)]-50=0\cdot 6$ which is nearer to the value for amylose. When the amount of bound iodine increases, because of the increase in the proportion of iodine bound by adsorption, $C_{\text{I}'}/C_{\text{I}}$) should increase if tri-iodide ions are adsorbed and decrease if iodine molecules are adsorbed The data (Table I) are inconclusive, for although they show an increase, it is within the limits of the experimental error.

The absorption spectra of the iodine complexes of tapioca, maize, waxy maize and sago amylopectins (Figs. 10 and 11) depend upon the amount of iodine bound in a similar manner to the spectra of potato amylopectin-iodine complexes. The maximum extinction coefficients diminish, and the absorptions at lower wavelengths increase with increasing iodine content, suggesting a concurrent increase in the proportion of iodine bound by adsorption. The salient features of the spectra are summarised in Table III. There are very close similarities between tapioca and maize amylopectins, and between sago and waxy maize amylopectins.

Table III

Amylopectin	3% Iodine bound			12 5% Iodine bound		
	$\varepsilon_{\max}$ $\times 10^{-4}$	ε_{4000} $\times 10^{-4}$	Wavelength of max abs Å	$\varepsilon_{\max}$ $\times 10^{-4}$	ε_{4000} $\times 10^{-4}$	Wavelength of max abs. Å
Potato	2 70	1 25	5400	2 40	1·50	5400
Tapioca	2 25	1·60	5300	2 00	1·70	5350
Maize	2 30	1 65	5400	2 00	1·70	5300
Waxy maize	1 90	1·63	5300	1 82	1 75	5350
Sago	1 95	1 75	5300	1·78	1·75	5300

The data have been analysed in the manner described on p 803 The values of x (Table IV) indicate that the proportion of iodine bound by helix formation varies, being less for sago and waxy maize than for maize and tapioca and largest for potato amylopectin. The calculated absorption spectra of the helix components of the different amylopectins (Figs. 12 and 13) are remarkably similar in view of the large differences between the

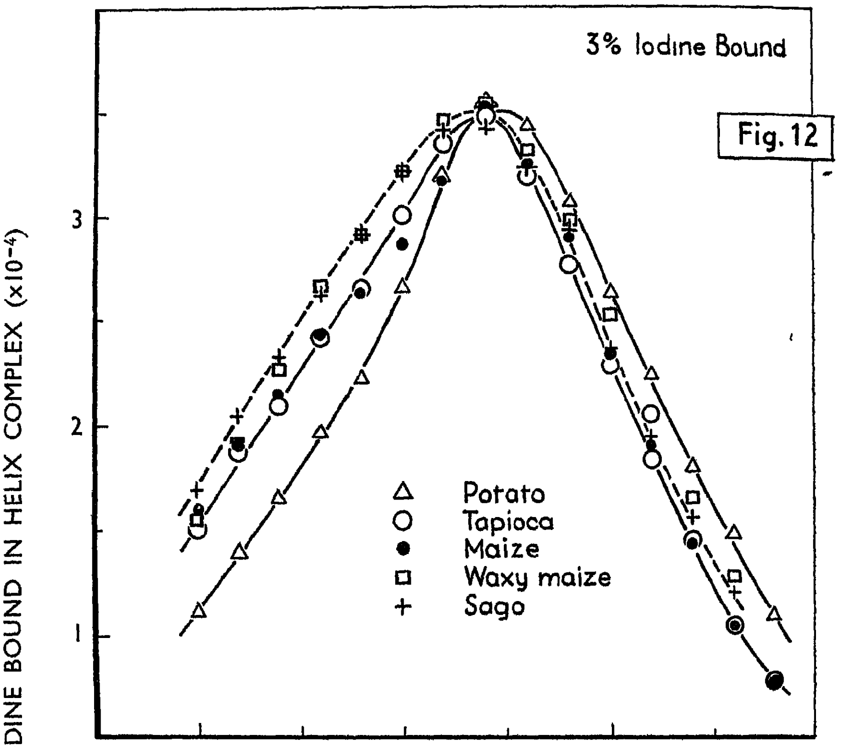


Fig. 12

3% Iodine Bound
3
2
1
Potato
Tapioca
Maize
Waxy maize
Sago
MOLECULAR EXTINCTION COEFF. OF IODINE BOUND IN HELIX COMPLEX (x10⁻⁴)

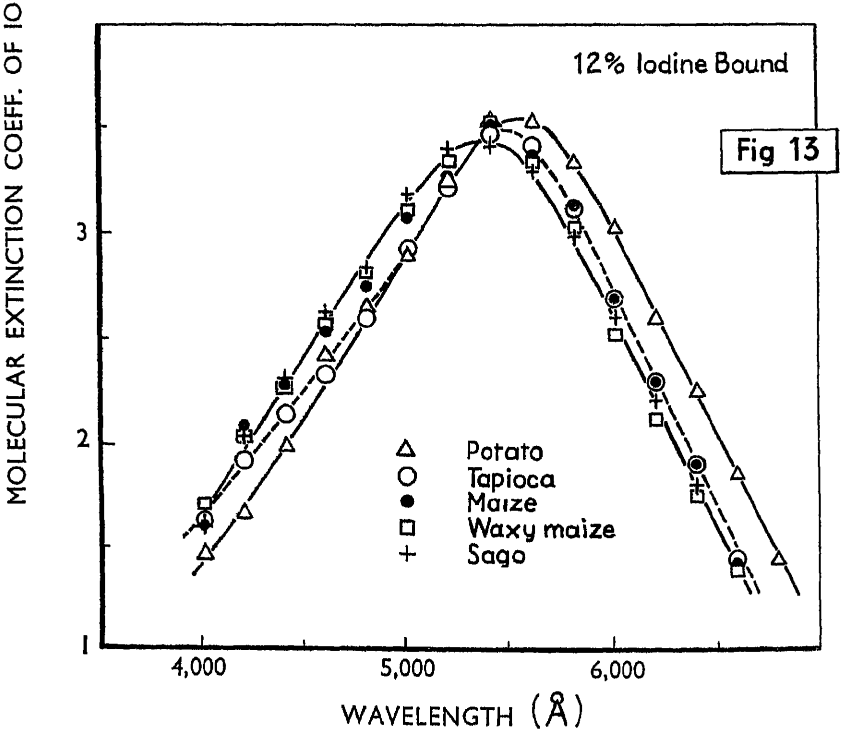


Fig 13

12% Iodine Bound
3
2
1
Potato
Tapioca
Maize
Waxy maize
Sago
4,000
5,000
6,000
WAVELENGTH (Å)

original spectral absorption curves. The differences between them suggest that the average length of the branches taking part in helix formation varies, being least for sago and waxy maize amylopectins, and greatest for potato amylopectin. Tapioca and maize amylopectins occupy an intermediate position, but resemble sago and waxy maize amylopectins more closely than they do potato amylopectin.

Table IV

Amylopectin	x for 3% iodine bound	x for 12·5% iodine bound
Potato	26	36
Tapioca	40	49
Maize	39	49
Waxy maize	53	55
Sago	50	56

If the proportion of iodine bound by adsorption varies among the different amylopectins, there should be concurrent variations in the ratios of the amounts of iodide and iodine absorbed. Unfortunately, this ratio cannot be determined for the complexes (containing 3 per cent. or 12·5 per cent. of iodine) to which the spectrophotometric data refer. The data for complexes containing 22 per cent. to 23 5 per cent. of iodine (Table II) suggest, however, that there is a variation, and that the proportion of iodide bound is higher for maize, sago and tapioca amylopectins than for potato amylopectin. This is in accord with the view that the adsorbed iodine is present in the form of tri-iodide ions

In conclusion, some mention must be made of the relation between the behaviour of amylopectin-iodine complexes and the average sizes of the repeating units in the amylopectins. Halsall, Hirst and Jones[1] have determined the sizes of the repeating units in a number of amylopectins, including the preparations of sago amylopectin and waxy maize amylopectin used in the present investigation. The results (Table V) suggest that there is no definite correlation between either the affinities for iodine of the amylopectins or the absorption spectra of their iodine complexes, and the average sizes of their repeating units, nor is such a correlation necessarily to be expected.

Table V

Amylopectin	Average number of glucose residues in repeating unit
Potato	20-23
Tapioca . . .	20
Maize	18·5
Sago	18
Waxy maize ...	20

EXPERIMENTAL

Materials

The preparation of sago, maize, tapioca and potato amylopectins has been described elsewhere,[12] some of their properties are summarised in Table VI. The waxy maize starch was a commercial sample. It contained 0·5 per cent. of amylose Before use, it was extracted with hot 85 per cent methanol, and washed thoroughly with water.

Table VI

Amylopectin	Amylose content %	Intrinsic viscosity of triacetate in nitroethane solution (concentration expressed as g. solute per 100 ml. solution)
Potato	1·8	1·66
Tapioca	1·1	1·40
Maize	6·3	1·28
Sago	1·0	1·06
Waxy maize	0·5	1·35

Preparation of Solutions

The amylopectins and glycogen were dissolved in boiling water. Waxy maize starch (5 g.) was gelatinised in water (250 ml.) saturated with butanol, the paste was heated at 126° C. for two hours to complete the dissolution of the starch, and the butanol was then removed by evaporation, fresh water being added as required. All solutions were used within two days of preparation. Their concentrations were determined by wet combustion with potassium dichromate and sulphuric acid,[13,14] a correction being applied to allow for the low result (98 per cent. of theoretical) given by this method.

Examination of the Iodine Complexes

The methods employed were identical with those previously used for amylose-iodine complexes, and described in detail in Part III[8] of the present series of papers.

Much of the experimental work has been carried out by Miss M. M. Bridges.

REFERENCES

[1] Halsall, Hirst and Jones. *J. Chem. Soc.*, 1948, 27.
[2] Meyer. "Advances in Colloid Science," Vol. I, New York, 1942.
[3] Haworth, Kitchen and Peat. *J. Chem. Soc.*, 1943, 619.
[4] Bourne, Haworth, Macey and Peat. *J. Chem. Soc.*, 1948, 924.
[5] Meyer and Bernfeld. *Helv. Chim. Acta*, 1940, 23, 875.
[6] Hodge, Montgomery and Hilbert. *Cereal Chem.*, 1948, 25, 19.
[7] Bates, French and Rundle. *J. Amer. Chem. Soc.*, 1943, 65, 143.
[8] Higginbotham, Part III of this series (preceding *Memoir*).
[9] Foster. *Iowa State Coll. J. of Science*, 1943, 18, 36.
[10] Swanson. *J. Biol. Chem.*, 1948, 172, 825.
[11] Baldwin, Bear and Rundle. *J. Amer. Chem. Soc.*, 1944, 66, 111.
[12] Higginbotham and Morrison. *Shirley Inst. Mem.*, 1948, 22, 148, and *J. Textile Inst.*, 1949, 40, T208.
[13] Birtwell and Ridge. *Shirley Inst. Mem.*, 1928, 7, 37, and *J. Textile Inst.*, 1928, 19, T341.
[14] Richardson, Higginbotham and Farrow. *Shirley Inst. Mem.*, 1935, 14, 63, and *J. Textile Inst.*, 1936, 27, T131.

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49—A NOTE ON THE THEORY OF THE LEPIDOMETER

By K Rachel Makinson

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An instrument much used in the study of the frictional properties of the wool fibre and their relation to felting is the lepidometer, developed by Speakman, Chamberlain and Menkart.[1] In this instrument, the fibre "is placed between two surfaces, which are caused to reciprocate under standard pressure" along the length of the fibre. The tip end of the fibre is attached to a torsion balance. "Fibre travel (towards the root end) proceeds until the tension developed in the measuring device (the torsion balance) is sufficient to arrest motion, and the maximum tension developed is taken as a measure of scaliness."

It is clear that this tension depends on the difference between the coefficients of friction of the fibre with and against the scales, and is related to the felting properties of the fibres As Speakman and his colleagues state, the lepidometer measures the "creeping power" of the fibre under a rubbing action. However, to correlate lepidometer measurements successfully with frictional measurements made by other workers, it is necessary to express in physical terms the quantity which is measured by this instrument. It is shown below that, in general, the instrument as used by Speakman *et al.*[1] measures a quantity which is greater than the difference σ_{ss} between the coefficients of static friction against and with the scales, lying between σ_{ss} and the difference σ_{sk} between the against-scale coefficient of static friction and the with-scale coefficient of kinetic friction The lepidometer therefore exaggerates small frictional differences, particularly under conditions such that the difference between static and kinetic friction is large.

The Action of the Lepidometer

The following nomenclature will be used:

μ = coefficient of friction between fibre and rubbing surface.
F = corresponding frictional force
x = distance of fibre travel at any time.
x_m = maximum value of x in any one oscillation of fibre.
x_n = minimum value of x in any one oscillation of fibre.
$f(x)$ = restoring force due to torsion balance.
$\sigma = \mu_2 - \mu_1$

Subscript 1 indicates rubbing towards the tip of the fibre
Subscript 2 indicates rubbing towards the root of the fibre
Subscript *s* indicates static friction.
Subscript *k* indicates kinetic friction.

Hence $\sigma_{sk} = \mu_{2s} - \mu_{1k}$, and similar relations hold for σ_{ss}, σ_{kk} and σ_{ks}.

Fig 1(a) illustrates schematically the principle of the lepidometer Numerical data are given by Speakman *et al.*[1] The rubbing surfaces were made of various materials, certain rubbers and polythene being most used. The space between the surfaces was filled with air or with the liquid in which the "scaliness" was to be measured.

In an analysis of the action of the lepidometer, two extreme cases may be considered. In both cases the force exerted on the torsion balance at any instant is equal to the tension in the wool fibre, in the first case, in which the damping and inertia of the torsion balance may be considered negligible, the balance will indicate this tension exactly; in the second case, when the damping and inertia are large, the balance will indicate only the mean value of this tension

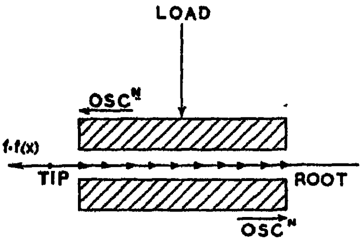

Fig. 1(a)
Conditions existing in the lepidometer.

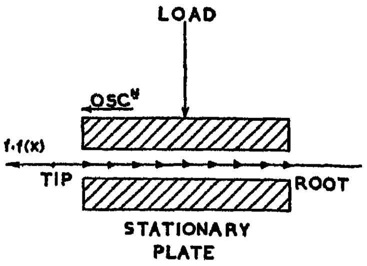

Fig. 1(b).
A similar but simpler case.

The principles involved in the first case may be illustrated by considering first the simpler system shown in Fig. 1(b), which differs from the lepidometer in that only one plate oscillates. Consider the first stroke of the upper plate to the left in Fig. 1(b). Initially $f(x)=0$ since $x=0$. The frictional force on the fibre to the left, due to the upper plate, can increase up to F_{1s}. That to the right, due to the lower plate, can increase up to F_{2s}, which is greater than F_{1s}. The fibre therefore remains stationary, and the frictional force between it and the upper plate drops to F_{1k}. The frictional force between the fibre and the lower plate then also drops to F_{1k}, so that equilibrium is maintained, and the fibre remains stationary throughout this stroke.

Consider now the first stroke of the upper plate to the right. Initially $f(x)=0$, the frictional force on the fibre to the right $\leqslant F_2$, and that to the left $\leqslant F_{1s}$. The fibre therefore moves to the right at the same speed as the upper plate, and the frictional force to the left falls to F_{1k}. The fibre travel continues until $x=x_m$, such that

$$F_{2s}=f(x_m)+F_{1k} \quad \ldots\ldots \quad \text{(i)}$$

Slip then begins between the fibre and the upper plate, so that the frictional force to the right falls to F_{2k} The fibre is rapidly decelerated until it comes to rest relative to the lower plate There will be no significant change in x during this rapid deceleration Just after the fibre has come to rest, the total force to the right is $\leqslant F_{2s}+F_{2k}$, while that to the left is $f(x_m)$ From (i) it can be seen that $F_{2s}+F_{2k}>f(x_m)$; the fibre therefore does not slip back. This equilibrium is readily seen to be stable so long as $2F_{2k}>F_{2s}-F_{1k}$; measurements made here[2,3] have shown that this is always true for wool rubbing on horn, and it may be expected to be true for wool on other surfaces.

Consider now the second stroke of the upper plate to the left. Just after reversal of its motion, when the upper plate is momentarily at rest, the force to the left $\leqslant f(x_m)+F_{1s}$ and that to the right $\leqslant F_{2s}$. From (i) it can be seen that $F_{2s}<f(x_m)+F_{1s}$. The fibre therefore moves to the left with the same speed as the upper plate. The force to the right then falls to F_{2k}, and the fibre continues to move to the left until $x=x_n$, such that

$$f(x_n)+F_{1s}=F_{2k} \ldots\ldots\ldots\ldots \quad \text{(ii)}$$

The fibre then comes to rest relative to the lower plate. It can readily be seen that this second equilibrium is stable.

During further oscillations of the rubbing surfaces the fibre oscillates between the displacements x_m and x_n. The exact values of x_m and x_n will, however, vary from cycle to cycle, since the coefficients of friction are not closely reproducible Any differences between or irregularities in the two rubbing surfaces will also appear as variations in the oscillations. The mean displaced position $(x_m+x_n)/2$ of the fibre corresponds, if $f(x)$ is a linear function of x, to $(F_{2s}+F_{2k}-F_{1s}-F_{1k})$.

If a similar analysis is now made of the conditions existing in Fig. 1(a), it is readily seen that the fibre again oscillates between the displacements x_m and x_n, but at a higher frequency. This increase in frequency is due to the fact that there is no stable equilibrium at the extreme positions x_m and x_n, so that the fibre performs several cycles during each half cycle of the plate-oscillation. {The number of fibre cycles per half plate-cycle approximates, when (x_m-x_n) is much less than the amplitude A of either plate, to $A/(x_m-x_n)$.}

Hence, since μ is proportional to F, the following conclusions may be drawn for the case when damping and inertia of the torsion balance are small: the balance executes oscillations about a mean displaced position corresponding to $(\sigma_{ss}+\sigma_{kk})/2$, the peak displacement corresponds to σ_{sk} and the trough to σ_{ks}.

The second extreme case to be considered is that in which the damping on and the inertia of the torsion balance are large. In this case, the torsion balance will register, after the initial rise, only a steady displacement corresponding to $(\sigma_{ss}+\sigma_{kk})/2$.

It may therefore be concluded that, in general, the torsion balance of the lepidometer will execute oscillations about a mean displaced position corresponding to $(\sigma_{ss}+\sigma_{kk})/2$. The peaks of these oscillations will correspond to some value between $(\sigma_{ss}+\sigma_{kk})/2$ and σ_{sk}. It has usually been found here[2,3] that σ_{ss} is very nearly equal to σ_{kk}; hence it follows that the peaks of the lepidometer trace correspond to a value greater than σ_{ss}.

This analysis has been based on the assumption that, in the range of velocities occurring in the lepidometer, the variations of friction with velocity can be represented by a definite coefficient of static friction and a (usually smaller) coefficient of kinetic friction which is independent of velocity. If this is not true the motion of the fibre becomes much more complicated. Such a representation has previously been shown[3] to be reasonable for wool rubbed on horn at velocities up to the order of 1 cm./sec Other workers[4,5] have shown for various surfaces that the coefficient of friction drops very rapidly from its static value to a much lower value as the velocity increases slightly from zero. Thereafter, any change with velocity is much slower. The approximation made here is therefore probably applicable to the lepidometer.*

Application to Measurements made with the Lepidometer

(1) The most important conclusion from this analysis is that lepidometer measurements will exaggerate small frictional differences, relative to measurements of σ_{ss} or σ_{kk}. It can be seen that, so long as there is any finite frictional difference at all, even if it is small, the "scaliness" measured by the lepidometer may be quite large, if the static and kinetic coefficients of friction are widely different and if the damping and inertia of the torsion balance

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*A few substances[6] show no definite static friction, but an initial slight increase in friction with velocity up to a maximum value If this were the case here, we should have to replace μ_s by this maximum value. The same correction would apply to μ_s measured by any of the usual methods. Wool on horn shows no such effect.

are not too high. This statement does not deny the possibility that some such factor as "scaliness" may be the factor which is directly related to feltability; in fact, it seems probable that in a mathematical study of felting σ_{sk} would be found to be important. It may, however, explain the fact that Speakman[1] obtains a smaller decrease in the "scaliness" after chlorine treatment than the decrease in σ_{ss} which is found by some other workers [7,8,9] However, it is difficult to make these comparisons, as the conditions of cleanliness, which are very important in frictional work, will have differed in different laboratories.

(2) When the fibres are lubricated $\sigma_{sk} \simeq \sigma_{ks}$, so that the oscillations of the torsion balance will become small. For well lubricated fibres, since μ_s and μ_k are nearly equal, it is immaterial (except when σ is very small) whether σ_{sk}, σ_{ks}, σ_{ss} or σ_{kk} is measured.

(3) Measurements made here for wool rubbed on horn show that, in general, $F_{2k} > F_{1s}$, so that from (ii), $f(x_n) > 0$. $f(x_n)$ is likely to be negative only in cases where σ_{ss} and σ_{kk} are small.

(4) Martin's[10] instrument for detecting frictional difference can be regarded as an extension of the principle of the lepidometer to the case where $f(x) = 0$ at all x. The fibre will therefore in this instrument migrate indefinitely towards its root end, so long as it has a finite frictional difference. Exceptions to this may occur if $\mu_s \simeq \mu_k$ and σ is small.

ACKNOWLEDGEMENTS

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SUMMARY

The quantity which is measured by the peaks of the lepidometer trace lies between the difference σ_{ss} between the coefficients of static friction with and against the scales and the difference σ_{sk} between the against-scale coefficient of static friction and the with-scale coefficient of kinetic friction. Since, except in the case of heavy lubrication, $\sigma_{sk} > \sigma_{ss}$, the quantity measured is greater than σ_{ss}, so that the instrument exaggerates small frictional differences. It is probable, however, that the particular quantity which it measures is related to the tendency of the mass of fibres to felt, the closeness of this relation depending upon the mechanical constants of the lepidometer.

REFERENCES

[1] Speakman, J. B., Chamberlain, N. H. and Menkart, J., *J. Textile Inst.*, 1945, 36, T91.
[2] Mercer, E H. and Makinson, K R., *ibid* , 1947, 38, T227.
[3] Makinson, K. R , *ibid.*, 1947, 38, T332
[4] Sampson, J B , Morgan, F., Reed, D. W. and Muskat, M., *J. App. Phys.*, 1943, 14, 689.
[5] Bristow, J R , *Proc Roy. Soc.*, *A*, 1947, 189, 88
[6] Papenhuyzen, P J , *Ingenieur* (*Utrecht*), 1938, 53, 75.
[7] Mercer, E H , *Nature*, 1945, 155, 573
[8] Lindberg, J. and Gralén, N., *Textile Res. J.*, 1948, 18, 470
[9] Lindberg, J and Gralén, N., *Nature*, 1948, 162, 112
[10] *W I R A Bull* , 1941, 9, 4

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50—THE ACTION OF DOFFERS AND FANCIES ON A WOOLLEN CARD*

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1. INTRODUCTION

An earlier paper[1] described a series of experiments made to investigate the interaction of workers and swifts when carding wool. The present paper describes a similar series of investigations on the behaviour of doffers and fancies.

Just as the experimental methods of investigating the behaviour of workers were novel ones, in that they introduced the idea of measuring their "Collecting Power", so the experimental work described here on doffers and fancies is also novel as it involved building a new carding unit erected on pedestals to such a height that a worker and stripper could be mounted *underneath* the swift The efficiency of the fancy and doffer in clearing the swift was then examined under various operating conditions by measuring the amount of wool which escaped their doffing action and which was collected underneath the swift by the underslung worker.

The action of a doffer is very similar to that of a worker, the only differences between the two being that the relative surface speed of doffer and swift is generally rather less than that between worker and swift and secondly the arc of contact is greater at the doffer. These differences are of degree only, and it is to be expected that the behaviour of doffers in clearing wool from cylinders will be similar to that of the workers already described,[1] and in particular that their collecting powers will increase with closer setting and, more markedly, with increased doffer speeds.

This was demonstrated quite simply in the first experiment using the single carding part specially built to enable observations to be made on the wool passing the doffer and travelling round to the feed rollers again under the swift.

This machine consisted of a 50 in swift, fitted with four 8 in workers and 3½ in. strippers, a 12 in. fancy and a 32 in doffer, all clothed with fillet clothing. The feed to this was by means of a feed lattice of adjustable speed, and the doffer was stripped by a fly-comb. In all these respects the outfit was a normal one, it differed from the usual arrangement in that a normally clothed worker and a stripper were slung in adjustable, but rigid, bearings underneath the swift and, in order that this could be done and at the same time be accessible, the framework was erected on reinforced concrete pedestals 18 in. high. The underslung worker (set with a 30 gauge) was driven by the ordinary worker chain whilst all the workers were driven independently of the doffer so that the speed of the latter could be adjusted without affecting any other carding conditions.

The idea underlying the use of this underslung worker was that wool which escaped the doffer would be worked by it on the under-side of the swift in the same way as the ordinary workers worked the wool on the top of the swift, and that it would thereby collect a fraction of the wool passing on the underneath side of the swift on its way back to the feed-rollers. Most carders who saw this underslung worker in action were surprised at the amount which it collected in normal running, it generally carried almost as much wool as the last worker on the top of the machine—a fact which indicated the very imperfect clearing action of a doffer in normal operation.

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* A description of work carried out at the Wool Industries Research Association.

Although it was realised that the underslung worker would not collect all the wool passing it, as long as its setting and speed were kept constant it was found that the amount of wool collected was very nearly proportional to the rate of flow of wool *past* the doffer, therefore the amount of wool collected, for different running conditions of doffer setting and speed, was used as an index of doffer efficiency under these conditions—a little wool on the worker indicating little wool passing the doffer and, therefore, a high doffer efficiency, and *vice versa.*

In this way the efficiency of the clearing action of the doffer was investigated, but it must not be forgotten that this is also dependent on the action of the fancy. In the first simple experiment the conditions under which the fancy operated were kept constant and this first experiment gave interesting results on the way in which the doffer behaved when wool was presented to it in one particular fashion. In the second experiment the clearing efficiency was examined with both doffer and fancy speeds varying. It was also found that the efficiency was affected by rate of feed to the card so this was varied and the way in which all these three variables combined to influence clearing efficiency was worked out.

The results obtained were confirmed as being generally true by a further series of tests using five different fancies.

The complete experiment gave a self-contained and consistent picture of the way in which clearing efficiency varied from one set of extreme running conditions to the other. The complete story is rather involved, but it is hoped that the paper makes it clear, because there is no doubt that effective clearance of the swift is one of the most important considerations for a carding engineer, not only from the point of view of "getting the wool away" and doing good work, but also from the point of view of reducing the need for fettling.

Differences of opinion exist regarding the way in which a fancy must be run to give the most efficient results The present paper shows that there is no one best set of running conditions for a fancy, but that the best conditions depend on rate of feed and the method of operating the doffer. It is therefore hoped that this paper will resolve some of the differences of opinion and show that two or more different views may be equally correct when other circumstances are taken into account.

In order to avoid the repetition of the phrases weight of wool on the first worker, weight of wool on the second worker, *etc.*, throughout this paper, these weights in any test are briefly referred to as follows —

Weight of wool on 1st top worker in grams	m_1
Weight of wool on 2nd top worker in grams	m_2
Weight of wool on 3rd top worker in grams	m_3
Weight of wool on 4th top worker in grams	m_4
Weight of wool on underslung worker in grams	m_5

2. EXPERIMENTAL OBSERVATIONS

Experiment I

The effect of doffer settings and doffer speeds on clearing efficiency when a particular method of fancy operation was adopted

Factors which were constant throughout the test.

Swift speed 84 r.p.m.
Workers' speed 4·5 r.p.m.
Fancy speed 406 r.p.m.
Worker and fancy settings.

During this test alterations were made to the doffer setting and doffer speed and wool was put through at two rates of feed, namely, 5·1 and 10·2 lb./hr.

Blend used: Equal parts of Australian lambs' wool, botany noils and scoured Australian pieces, plus 10 per cent. oleine.

The blend was scribbled by the Garnett breast and the first two swifts of another carding machine and taken off as a broad thick lap of well scribbled wool from the Tatham feed. This lap was cut into 60 in. lengths which were laid cross-wise on the feed sheet of the experimental carding unit. They were weighed before using and they were all adjusted to the same weight—by stripping off one or more layers of the lap—before feeding, thus ensuring a uniform rate of feed into the machine.

Wool was fed in until conditions were judged to be steady; the running time to ensure this was determined by a series of preliminary trials. The machine was then stopped and the wool carried on the underslung worker was removed by operating the worker and stripper by hand. This wool was then weighed—m_5. The average value of m_5 in three such tests under the same conditions of operation was taken as the index of the efficiency of the doffer under those conditions.

Table I shows how m_5 varied with doffer setting, doffer speed and rate of feed.

Table I

m_5

(1)	(2)	(3)	(4)	(5)	(6)
Rate of feed—lb./hr.	Doffer speed r p.m.	Doffer setting			Mean
		26 gauge	28 gauge	30 gauge	
5·1	10·0	7·7	7·9	6·6	10·0
10·2	10·0	14·0	12·9	10·8	
5·1	4·5	10·8	9·2	7·4	12·7
10·2	4·5	18·7	17·1	13·2	
	Mean	12·8	11·8	9·5	

Conclusions

The following conclusions can be drawn from these results:—

(1) A higher doffer speed gives a smaller value of m_5 and therefore indicates a higher doffer collecting power. This is true at all settings and at both rates of production. (Column (6) in the table shows the average effect of doffer speed, 27 per cent. more material is collected by the underslung worker when the speed is reduced from 10 r.p.m. to 4·5 r.p.m.).

(2) Closer doffer setting gives increased collecting power. This is true at both speeds and both rates of production (The last horizontal row of figures shows the average effect of doffer setting, there is about 33 per cent. more material collected on the underslung worker when the doffer setting is opened out from a 30 gauge setting to a 26 gauge setting.)

(3) From the above results it will be seen that the speed increase has been almost as effective in improving the collecting power of a doffer as has setting 4 gauges closer.

(4) There is a considerable difference in behaviour between the two extreme conditions, m_5 varying from 18·7 to 10·8 at 10 lb./hr. and from 10·8 to 6·6 at 5 lb./hr.

(5) As doubling the rate of feed in no case doubles the value of m_5 this suggests that the doffer clears more effectively at higher rates of feed.

Experiment II

The effect of doffer speeds, fancy speeds and rate of production on the clearing efficiency

The results of Experiment I were amplified by a second series of tests carried out on five different blends of wool on the same machine.

Factors which were constant throughout the test.

Swift speed, 84 r.p.m.
Workers' speed, 4·5 r.p.m.
Workers' setting to swift.
Fancy setting to swift.
Doffer setting to swift.

Factors varied throughout test.

(1) Doffer speeds—4·5 to 10 r.p.m.
(2) Fancy speeds 342 to 406 r.p.m. at the two extreme doffer speeds.
(3) Rates of feed 10 to 40 lb./hr at all speeds of doffer and fancy
(4) Blend of wool.

Table II

Blends used in Experiment II

Blend No.	50/50 blend of
D.1	Scoured Australian lamb's wool 64s Scoured Australian locks.
D.2	Scoured 56s/58s. Scoured 50s.
D 3	Scoured N Z. locks 46s/50s. Scoured N Z bulky pieces 48s/50s
D.4	Scoured Australian 64s 2 in. staple. Scoured Australian 64s 3½ in staple
D 5	Botany noils 64s Cross-bred noils 50s/56s

The test procedure was exactly the same as in Experiment I, the wool was oiled with 10 per cent. of oleine and scribbled on the Garnett breast and first two swifts of another machine; 60 in. lengths of Tatham feed lap of constant weight were fed cross-wise on the feed lattice of the experimental unit card.

The rates of feed 10, 20, 30 and 40 lb./hr. are more closely related to normal working conditions than in Experiment I where low rates of feed (5 and 10 lb./hr.) had been adopted.

The tests carried out were designed to measure the changes in m_5 as the rate of feed, doffer speed, fancy speed and type of blend were varied. In addition under many of the test conditions the amount of wool carried by the four top workers (m_1, m_2, m_3, and m_4) was determined as it was thought that a study of the load of wool on the top of machine in these various circumstances would also be interesting.

The results obtained are given in Tables III to VI, and for easier appreciation are illustrated graphically in Figs. 1-4.

The top half A, Table III and Figs. 1 and 2 show the values of m_5 found for various rates of feed at 5 doffer speeds with a fixed fancy speed—406 r.p.m. for blend D 1 and 342 r.p.m. for blends D.2 to D 5 inclusive.

Table III

m_5—Weight of wool in grams on underslung worker—Effect of doffer speed and rate of feed

	Blend	D.1 Fancy 406 r p m					D 2 Fancy 342 r p m					D 3 Fancy 342 r p m					D 4 Fancy 342 r p m					D 5 Fancy 342 r.p m.					Means m_5 for blends D 2-D 5					
	Doffer speed r p.m / Feed lb /hr.	4·5	5	6·3	7	10	4·5	5	6·3	7	10	4·5	5	6·3	7	10	4·5	5	6·3	7	10	4·5	5	6·3	7	10	4·5	5	6·3	7	10	
A	10	22·0			13·5	12·6	20·3	19·0	20·8	18·8	15·9	18·9	18·5	18·5	16·8	14·5	22·2	20·9	22·0	19·0	19·0	12·9	11·8	12·9	11·8	11·9	18·6	17·6	18·6	16·6	15·3	
	20						39·8				35·0	36·2				31·9	35·5				27·5	21·4				17·8	33·2				28·2	
	30	52·5	40·5	36·5	34·0	31·5	59·8	55·2	55·0	47·2	44·8	54·9	49·0	49·4	44·4	43·0	48·4	45·6	43·9	40·4	36·1	31·3	28·4	28·8	25·3	23·1	48·6	45·9	44·4	39·3	36·9	
	40	69·5	53·5	50·0	43·5	38·7	74·3	73·4	70·6	66·6	56·8	53·0	54·9	56·0	48·0	45·8	56·6	49·8	48·9	44·6	40·1	35·4	33·7	34·2	29·3	25·8	55·2	53·2	52·4	47·2	42·4	
		Weight of wool on underslung worker per unit rate of feed — $\frac{\text{grams}}{\text{lb /hr.}}$																														Mean for all doffer speeds and all blends
B	10	2·20			1·35	1·36	2·03	1·90	2·08	1·88	1·59	1·89	1·85	1·85	1·68	1·45	2·22	2·09	2·20	1·90	1·90	1·29	1·18	1·29	1·18	1·19	1·86	1·76	1·86	1·66	1·53	1·73
	20						1·99				1·75	1·81				1·60	1·78				1·38	1·07				0·89	*1·66				*1·41	1·53
	30	1·75	1·35	1·22	1·13	1·05	1·99	1·84	1·83	1·57	1·49	1·83	1·63	1·65	1·48	1·43	1·61	1·52	1·46	1·35	1·21	1·04	0·95	0·96	0·84	0·77	1·62	1·53	1·48	1·31	1·23	1·43
	40	1·74	1·34	1·25	1·09	0·97	1·86	1·84	1·77	1·67	1·42	1·33	1·37	1·40	1·20	1·15	1·42	1·25	1·22	1·12	1·00	0·89	0·84	0·86	0·73	0·65	1·38	1·33	1·31	1·18	1·06	1·25
																						Mean—omitting*					1·62	1·54	1·56	1·38	1·27	

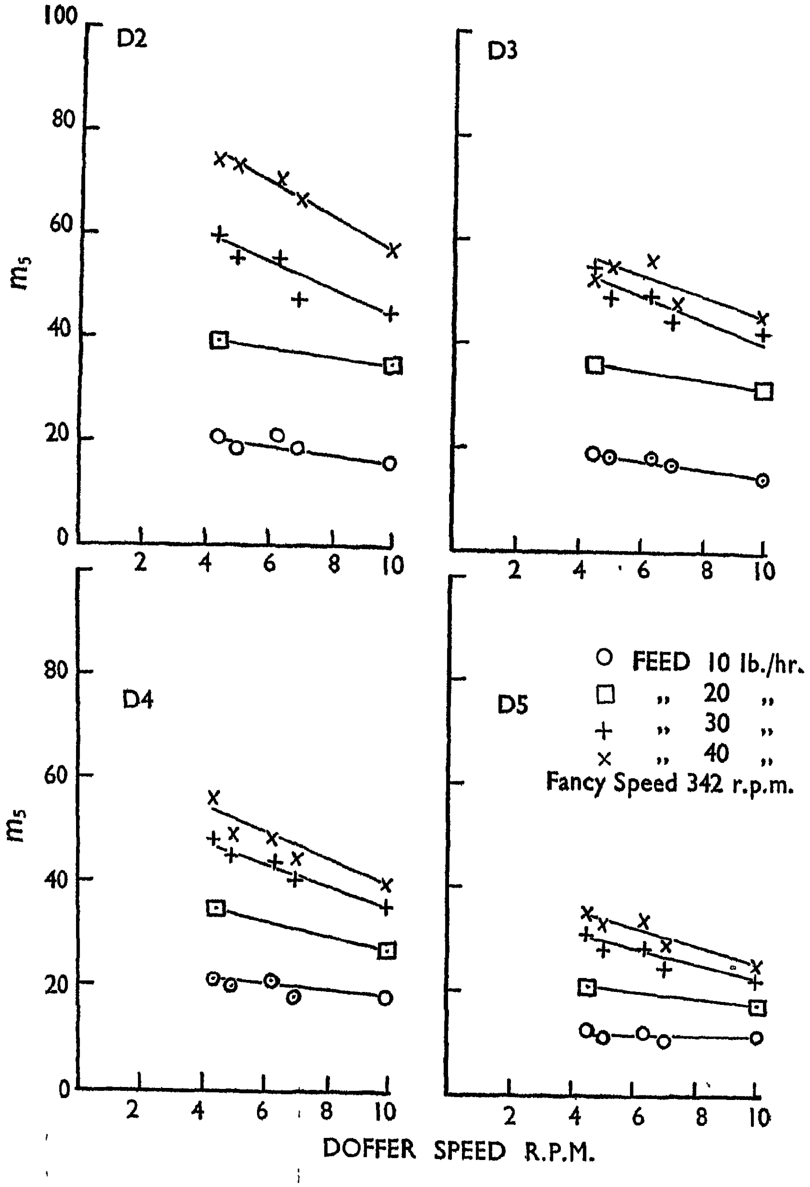

Fig. 1

At any rate of feed with all blends m_5 decreases as the doffer speed increases, this shows conclusively the validity of the conclusion reached after Experiment I, that the higher doffer speeds give an increased doffer collecting power, this is now seen to be true for all blends at all rates of feed.

The lower half B of Table III shows m_5 divided by the rate of feed, *i.e.* it is the weight of wool on this underslung worker per unit rate of feed into the machine. It will be seen that as the rate of feed into the machine increases from 10 to 40 lb./hr., the weight of wool on the underslung worker per lb /hr. flowing through the machine decreases, in other words the doffer takes a larger share and clears the swift more efficiently at the higher rates of

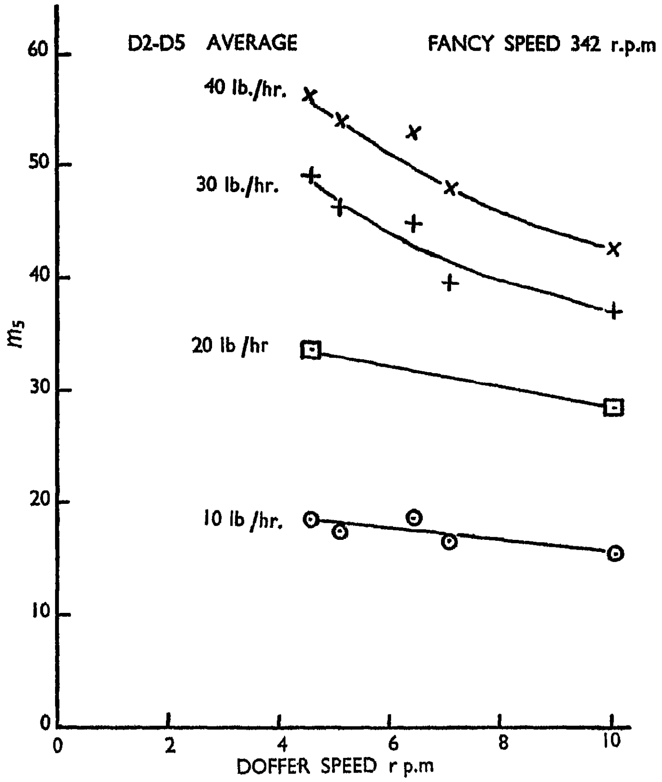

Fig 2

feed. This is true only at the particular fancy speeds quoted. It will be seen when considering Table IV that this behaviour is likely to vary somewhat according to the speed of the fancy.

The final line in the right hand bottom corner of Table III shows the average effect of dofter speed for all blends over all the rates of feed. With a doffer speed of 4·5 r.p.m. the underslung worker on the average carries 1·62 grams of wool per lb./hr. fed in, at a doffer speed of 10 r.p.m. it carries 1·27 grams for the same rate of feed; the ratio of the two—1·27—is exactly the same as that found in Experiment I.

Table IV and Figs. 3 and 4 show how m_5 varied as fancy speed was varied at the highest and lowest rates of feed (40 and 10 lb /hr.) using the two extreme doffer speeds (4·5 and 10 r.p.m.).

It will now be seen from section A of Table IV, in addition to what has already been said, that the fast moving doffer behaves more efficiently at *all* fancy speeds, with all blends at all rates of feed, m_5 being lower for a doffer speed of 10 r.p.m. than for a doffer speed of 4·5 r.p.m.

The data of Table IV—section A—also enable us to see that *in most cases* the doffer behaves more efficiently as the fancy speed is increased (m_5 decreases as fancy speed increases) This is true under all conditions save one—the condition of high rate of feed combined with a slow doffer speed (marked * in Table IV and Fig. 3). In these circumstances as the fancy speed increases the value of m_5 either remains approximately the same (D.1, D 4 and D.5) or increases (D 2 and D.3).

Table IV

m_5—Weight of wool in grams on underslung worker—Effect of fancy speed at 2 rates of feed and 2 doffer speeds

	Blend	R P.M.	D 1				D 2				D.3				D 4				D 5				Mean for blends D.2-D 5			
	Rate of feed lb /hr	Fancy Speed / Doffer Speed r p m	342	358	384	406	342	358	384	406	342	358	384	406	342	358	384	406	342	358	384	406	342	358	384	406
A	10	4 5	29 0	25 0	23 3	22 0	20 3	18 1	18 4	17 2	18 9	15 3	14 3	12 8	22 2	18 9	16 6	15·2	12·9	10 5	9 9	9 6	20 7	17 6	16 5	15 4
		10	19 0	17·1	14 2	12 6	15 9	14 3	12 8	10 9	14 5	13 4	11 7	9 5	19 0	16 2	13 0	11 2	11 9	9 6	7 8	7 6	16 1	14 1	11 9	10·4
	40	4 5*	67·0	67 5	67 0	69 5	74 3	78 9	83 4	84 2	53 0	57 6	63 6	62 1	56 6	51 9	57 2	56 7	35 4	35 6	36 9	37 0	57 3	58 3	61 6	61 9
		10	42 0	41 0	39 0	38 7	56 8	51 4	49 9	44 5	45 8	43·0	40 6	37 1	40 1	39 4	35 8	36 7	25 8	23 0	21·8	22 5	42 1	39 6	37 4	35 9
	Weight of wool on underslung worker per unit rate of feed — $\frac{\text{grams}}{\text{lb /hr.}}$																									
B	10	4 5	2 90	2 50	2 33	2 20	2 03	1 81*	1 84*	1 72*	1 89	1 53	1 43*	1 28*	2 22	1 89	1 66	1·52†	1 29	1 05	0 99†	0 96†	2 07	1 76	1 65†	1 54*
		10	1 90	1 71	1 42	1·26	1 59	1 43	1 28	1 09*	1 45	1 34	1 17	0 95†	1 90	1 62	1 30	1 12	1 19	0 96	0 78	0 76	1 61	1 41	1·19	1 04
	40	4 5	1 68	1 69	1 68	1 74	1 86	1 97*	2 09*	2 11*	1 33	1 44	1 59*	1 55*	1 42	1 30	1·43	1 42†	0 89	0 89	0 92†	0 93†	1 43	1 46	1 54†	1 55*
		10	1 05	1 03	0 98	0 97	1 42	1 29	1 22	1 11*	1 15	1 08	1 02	0 93†	1 00	0 99	0 90	0 92	0 62	0 58	0 55	0 56	1 05	0 99	0 94	0 90

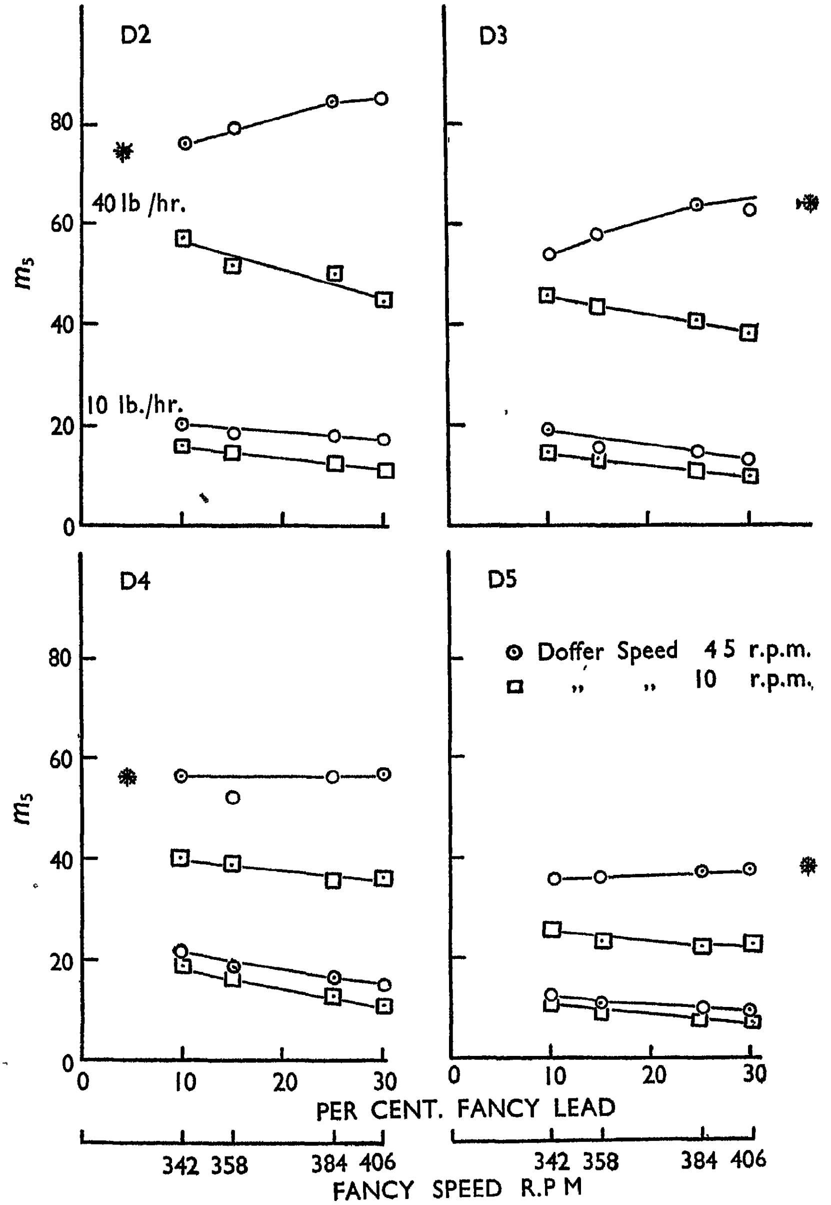

Fig. 3

This conclusion is seen in better perspective by considering the lower half—B—of Table IV, where the results are again reduced to the weight of wool on the under worker per unit rate of flow through the machine. Considering the mean figures for all blends at the bottom right hand corner of the Table, it will be seen that at a rate of feed of 10 lb /hr. and a doffer speed of 4·5 r.p.m. 2·07 grams of wool were found on the under worker per lb./hr. flowing through when the fancy was revolving at 342 r.p.m. At a fancy speed of 406 r.p.m. the corresponding amount was only 1·54 grams. The ratio of these two, representing the improvement in doffing action due to increased fancy speed, is 1·21. Similar ratios can be worked out for the other three conditions; the complete set is as follows:—

Table IVa

Rate of Feed—lb./hr.	$\dfrac{\text{Amount of wool on underslung worker—Fancy 342 r.p.m.*}}{\text{Amount of wool on underslung worker—Fancy 406 r.p.m.}}$	
	Doffer speed 10 r.p.m.	Doffer speed 4·5 r.p.m.
10	1·55	1·21
40	1·17	0·92

* Per lb./hr. entering

It will be seen therefore that when the swift was lightly loaded increase in fancy speed was effective. Anything which tends to load the swift more, either increasing the rate of feed or a low doffer speed (which prevents the swift being effectively cleared) reduces the benefits of a high fancy speed. The effectiveness of high fancy speeds became progressively less as the load on the swift increased. In the extreme case where the rate of feed was high and the doffer ran slowly a high fancy speed either made no difference or reduced the effectiveness of the lifting and clearing action.

This behaviour immediately calls attention to another result illustrated by the results in Table IV. It was said earlier in considering the results of Table III that for the particular fancy speeds quoted there as the rate of feed increases from 10 to 40 lb./hr. the doffer cleared the swift more efficiently,* but now having data which cover a wide range of fancy speeds, we note that this is not true in many cases (indicated by * in Table IV). These again are cases of overloading and occur most generally at low doffer speeds and high fancy speeds. Here the increased rate of feed instead of making the doffer more efficient makes it less efficient. Even in the cases where the clearing efficiency is not reduced we find that as these extreme conditions (marked † in Table IV) are approached the clearing efficiency with increased rate of feed is being impaired. This effect in fact is also a progressive one.

Let us consider the mean figures for all blends at the bottom right hand corner of the table. At a doffer speed of 4·5 r.p.m., a fancy speed of 342 r.p.m. and a rate of feed of 10 lb./hr. 2·07 grams of wool were found on the under worker for every lb./hr. flowing through the machine. At a doffer speed of 4·5 r.p.m., the same fancy speed of 342 r.p.m., but a rate of feed of 40 lb./hr., the corresponding amount of wool was only 1·43 grams. The ratio of the two, representing the increased efficiency of the doffing action at 40 lb./hr. is 1·45. These ratios can be worked out for all fancy speeds and both doffer speeds, the full set of these ratios for all the conditions summarised in Table IV is as follows:—

Table IVb

Doffer speed r.p.m.	$\dfrac{\text{Amount of wool on underslung worker at 10 lb./hr.}}{\text{Amount of wool on underslung worker at 40 lb./hr.}}$ per lb./hr. entering			
	Fancy speed r.p.m.			
	342	358	384	406
4·5	1·45	1·21	1·07	1·00
10	1·53	1·42	1·27	1·16

---

* This is not at variance with the remark made above that the swift tends to get loaded more at high rates of feed. *E.g.*, rate of feed 10 lb./hr, a doffer efficiency of 50 per cent. would mean 20 lb./hr. flowing over the top of the machine. Rate of feed 30 lb./hr., a doffer efficiency of 75 per cent. would mean 40 lb./hr. flowing over the top.

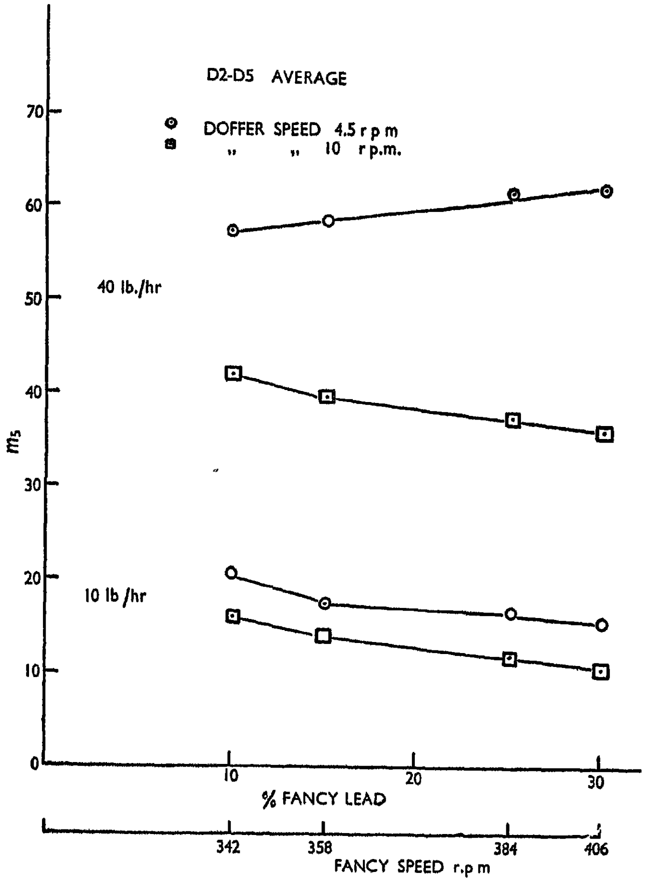

Fig. 4

Thus we can conclude that although the clearing action is more efficient at high rates of production the degree of improvement is affected by fancy speed and doffer speed, the effect (measured by the ratios in the above table) becomes progressively smaller at higher fancy speeds and lower doffer speeds (conditions promoting overloading of the swift) and may even be reversed with some blends.

Conclusions

We have therefore considered the effect of three factors on the efficiency with which the swift is cleared by the fancy-doffer combination These three factors are (*a*) doffer speed, (*b*) fancy speed and (*c*) rate of feed, and at this point we can summarise the conclusions reached as a result of this experiment. They can now be combined to give the following picture of what takes place

(1) The effect of increasing the doffer speed is to increase the efficiency with which the swift is cleared. This is true for all fancy speeds, at all rates of feed for all wools.

(2) The effect of fancy speed on the efficiency of clearing cannot be so simply stated because it varies according to doffer speed and rate of feed.

At high doffer speeds and low rates of feed (conditions which produce a light loading of the swift with wool) high fancy speeds cause the swift to be

Table V

Weight of wool on top workers in grams—Effect of fancy speed, doffer speed and rate of feed

		Blend	D 2				D.3				D.4				D.5				Average for blends D.2-D 5			
	Rate of feed lb./hr	Fancy speed r p m / Doffer speed r.p m.	342	358	384	406	342	358	384	406	342	358	384	406	342	358	384	406	342	358	384	406
1st Worker m_1	10	4·5	12·6	9·5	9·7	8·5	14·8	11·7	9·9	8·9	21·1	17·5	15·4	12·4	14·2	11·8	10·5	9·6	15·7	12·6	11·4	9·9
		10	9·9	8·9	6·9	5·0	11·9	9·7	8·7	6·4	20·7	17·0	13·4	11·4	16·6	12·8	9·9	8·7	14·8	12·1	9·7	7·9
	40	4·5	58·0	54·0	51·6	50·7	48·6	49·4	47·1	44·1	60·7	57·4	54·1	51·0	40·9	37·5	35·1	32·8	52·1	49·6	47·0	44·7
		10	48·3	42·7	39·5	34·3	48·9	42·6	37·5	35·8	53·3	49·1	43·7	41·9	36·2	29·0	26·0	24·7	46·7	40·9	36·7	34·2
2nd Worker m_2	10	4·5	12·6	9·4	9·3	8·3	14·4	10·8	9·4	8·0	20·2	16·7	14·6	11·5	14·3	11·7	10·5	9·6	15·4	12·2	11·0	9·9
		10	9·7	8·5	6·6	4·8	10·7	8·7	7·2	5·5	19·9	16·0	12·1	10·0	16·2	12·5	9·5	8·5	14·1	11·4	8·9	7·2
	40	4·5	60·8	55·0	53·8	51·6	48·2	48·8	46·4	43·5	62·6	58·6	56·0	51·2	41·8	35·2	36·4	35·0	53·4	49·4	48·2	45·3
		10	50·5	43·5	39·8	34·1	47·1	41·0	36·7	34·8	53·2	42·8	43·4	40·3	38·3	29·5	26·4	25·2	46·8	39·2	36·6	33·6
3rd Worker m_3	10	4·5	11·2	8·1	7·6	6·4	13·2	9·6	8·0	6·9	18·5	15·0	12·6	9·4	13·2	10·5	9·2	8·2	14·0	10·8	9·4	7·7
		10	8·3	7·1	5·2	3·6	9·6	7·6	6·0	4·8	18·0	13·8	10·2	8·2	15·0	11·0	8·2	6·9	12·7	9·9	7·4	5·9
	40	4·5	52·7	46·7	44·7	42·2	43·5	43·4	41·1	37·9	57·0	51·9	48·8	44·4	39·7	36·1	34·4	32·9	48·2	44·4	42·4	39·4
		10	43·4	36·5	32·5	27·8	41·2	36·0	31·7	29·4	47·3	42·8	36·8	34·3	33·9	27·5	23·8	23·1	41·5	35·7	31·2	28·7
4th Worker m_4	10	4·5	12·6	9·4	9·1	7·9	14·3	10·5	8·6	7·2	20·7	16·4	14·1	10·4	14·2	11·5	9·9	8·9	15·5	12·0	10·4	8·6
		10	9·2	8·4	6·9	5·6	10·2	7·9	8·7	6·5	20·0	15·4	11·3	8·9	16·1	11·6	8·8	7·5	13·9	10·8	8·9	7·1
	40	4·5	54·9	48·8	47·8	45·2	45·3	44·6	42·0	39·5	59·3	52·9	50·6	45·8	41·0	38·2	36·4	34·6	50·1	46·1	44·2	41·3
		10	46·9	38·5	34·3	29·7	43·4	37·8	33·0	31·5	49·4	44·3	37·9	35·5	35·1	28·7	24·8	23·8	43·7	37·3	32·5	30·1

more efficiently cleared than low fancy speeds. As rate of feed increases or doffer speed decreases the loading of the swift increases and the benefits of high fancy speed progressively diminish until, in the limit which combines the highest rate of feed with the slowest doffer speed, the clearing efficiency is unaffected by an increase in fancy speed for some wools and for others the clearing efficiency is reduced.

(3) Similarly the way in which the efficiency of clearing is affected by different rates of feed cannot be simply stated because it depends on both the doffer speed and fancy speed

At high doffer speeds (a condition which helps to get the wool away) and at low fancy speeds, increasing the rate of feed increases the clearing efficiency,* but as fancy speeds increase and doffer speeds decrease the benefit of a high rate of feed progressively diminishes until in the limit when both the doffer speed is low and the fancy speed is high the effect of increasing the rate of feed is to reduce the clearing efficiency with some wools and with other wools there is little effect.

(4) The optimum conditions for good clearing of the swift are therefore close doffer settings and high doffer speeds. Clearing is also proportionately more effective at high rates of feed In general higher fancy speeds are more effective at low productions and the higher doffer speeds, *i e.* when the swift is under conditions of light loading. As the load increases the benefit of increasing the lead of the fancy gradually disappears.

These are the main findings of this investigation which were confirmed by the further tests now to be described.

3. FURTHER EXPERIMENTAL OBSERVATIONS

Experiment III

During the course of Experiment II the main conclusions arrived at were confirmed by observations made on m_1, m_2, m_3 and m_4 which were determined for blends D.2-D.5 as set out in Table V.

To make the data more readily appreciated the average behaviour of *all four workers under all conditions* is shown in Table VI

Table VI

Mean behaviour of the four top workers carding blends D.2-D.5. Effect of fancy speed, doffer speed and rate of feed

Rate of feed lb /hr	Doffer speed r p m.	Average weight of wool on a worker in grams				Weight of wool on worker per unit rate of feed—lb /hr			
		Fancy speed r p m.				Fancy speed r.p.m			
		342	358	384	406	342	358	384	406
10	4·5	15·2	11·9	10·6	9·0	1 52	1 19	1·06	0 90
	10	13·9	11·1	8·7	7·0	1·39	1·11	0 87	0 70
40	4 5	51 0	47·4	45·5	42·7	1·28	1 19	1·14	1 07
	10	44·7	38 3	34 3	31 7	1 12	0 96	0 86	0·79

It will be seen that as the doffer speed was increased the load of wool on the top workers decreased

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* *Clearing efficiency, it must be emphasised, refers to the ability of the doffer and fancy to clear the wool going through the machine. Thus if it is stated—as above—that the clearing efficiency under certain conditions is greater the higher the rate of feed, it does not mean that there is less wool remaining on the swift when more is going through, but a smaller proportion of the amount being fed in unit time, say per revolution of the swift.*

As the fancy speed was increased the load on the workers decreased, but again the extent of the benefit gained by increased fancy speed depended on the running conditions. The ratio of the average amount of wool carried by the top workers at 342 and 406 r.p m. fancy speeds was 1·99 at a rate of feed of 10 lb./hr. and doffer speed of 10 r.p.m. For the four operating conditions the ratios were:—

Table VIa

$$\frac{\text{Average amount of wool carried by top workers—Fancy 342 r.p m.}}{\text{Average amount of wool carried by top workers—Fancy 406 r.p.m}}\ \text{(per lb./hr feed)}$$

Rate of feed lb./hr.	Doffer—10 r p.m.	Doffer—4·5 r.p.m.
10	1 99	1·69
40	1·42	1 20

Thus the results again show the progressively smaller effect of raising the fancy speed as conditions are approached which put higher loads of wool on the swift. These tests on the top workers, however, did not show the benefit to vanish entirely at the extreme condition of 40 lb./hr. rate of feed and doffer speed of 4·5 r.p.m, as was found when considering the results of m_5. To this extent the results of the two experiments are inconsistent.

The second half of Table VI shows the average values of m_1-m_4 reduced to the average weight per unit rate of flow of wool through the machine. This was done in order to compare the clearing efficiency of the fancy and doffer at 10 and 40 lb./hr. At a doffer speed of 4·5 r.p.m. and a fancy speed of 342 r.p.m. with a rate of feed 10 lb./hr. an average amount of 1·52 grams of wool was found on each worker per lb./hr. flowing through the machine. At 40 lb./hr. the corresponding amount was 1·28 grams indicating a lighter load on the top of the machine per unit rate of feed and consequently the greater clearing efficiency at 40 lb./hr The ratio of these two values, used as an index of the improved efficiency is 1·19. For the full range of operating conditions the full set of ratios indicating the relative clearing efficiencies at the two rates of feed is:—

Table VIb

$$\frac{\text{Average amount of wool on top workers at 10 lb /hr}}{\text{Average amount of wool on top workers at 40 lb /hr.}}\ \text{(per lb./hr. feed)}$$

Doffer speed r p m.	Fancy speed r p.m			
	342	358	384	406
4·5	1·19	1 00	0·93	0 84
10	1·24	1·17	1·32	1·35

These results are similar to, but not entirely consistent with those given in Table IV(b) when the behaviour of the underslung worker was under consideration, they again indicate, although not quite so conclusively, that the clearing action of the fancy and doffer is more efficient at high rates of production, but the degree of improvement is affected by fancy speed and doffer speeds, it becomes small at high fancy speeds and low doffer speeds.

Conclusion

The results on the top workers are such as substantially to confirm those obtained from the tests on the underslung worker.

There are differences in detail where exact agreement between the two sets of results is not found. Too much importance should not be attached to these differences, however, and the best interpretation of the behaviour of the fancy and doffer action is undoubtedly to be made from consideration of the results obtained from the underslung worker. This is because this worker deals only with wool escaping the action of the doffer whereas the amount of wool collected by the top workers will be determined not only by this, but also by their reaction to different rates of feed of new wool entering the machine. Thus in Table VI(b) the ratio of the amounts of wool per unit rate of feed collected by the top workers at different rates of feed will not only be affected by the different efficiencies of the doffer and fancy in clearing the swift under these two conditions, but possibly also by different behaviours of the top workers themselves in handling the wool at such different rates.

Tests on fibre length

During Experiment III samples of fibres were taken during the processing of blends D.2, D.3, D.4 and D.5 from (1) the last top worker and (2) from the carded web. These samples were all taken when the fancy was running at 358 r.p.m. at the high and low doffer speeds and at the high and low rates of feed.

About 1,000 fibres were measured from each sample taken and the mean fibre lengths found are given in Table VII.

Table VII

Mean fibre length—cm.

Fancy speed 358 r p.m.

Rate of feed lb /hr.	Doffer speed r p m.	D.2		D.3		D 4		D 5	
		Worker	Web	Worker	Web	Worker	Web	Worker	Web
10	4·5	3·80	3·24	3·45	3·15	3·33	2·93	1·78	1·63
	10	3·56	3·56	3·71	3·12	3·50	3·05	1·71	1·70
40	4·5	4·10	4·00	3·03	2·72	3·54	2·91	1·72	1·65
	10	4·08	3·59	3·01	3·03	3·37	2·87	1·78	1·62

Blend ..	Mean fibre length		Mean fibre length in carded web			
	Worker	Web	10 lb /hr.	40 lb./hr.	4·5 r p m	10 r p.m.
D 2	3·89	3·60	3·40	3·80	3·62	3·58
D 3	3·30	3·00	3·14	2·88	2·94	3·08
D 4	3·44	2·94	2·99	2·89	2·92	2·96
D 5	1·75	1·65	1·67	1·64	1·64	1·66
Mean	3·10	2·80	2·80	2·80	2·78	2·82

The detailed results are given in the top half of the table, but as the errors of fibre measurement of woollen blends are so great (the sampling error alone gives each figure quoted a standard error of 2 per cent.) the mean values worked out in the lower half of the table will be used to state the general conclusions of the test.

It is not surprising to find that the fibre length of the wool on the worker is greater than the mean fibre length in the emerging web. The worker will tend to collect those which protrude most prominently from the swift clothing and these will be long fibres.

Conclusion

The average fibre length in the carded web is unaffected by doffer speeds or rate of production. This is true of each individual blend. In this connection it should be remembered that the wool had been well scribbled before entering the machine

Table VIII

m_5—Weight of wool in grams on underslung worker—Effect of fancy speed and rate of feed for five different fancies

Doffer speed 10 r.p m.

	Fancy	F.1				F 2				F 3				F 4				F.5				Average m_5			
	Speed r p m / Rate of feed lb /hr.	342	358	384	406	342	358	384	406	342	358	384	406	342	358	384	406	342	358	384	406	342	358	384	406
A	10	10·9	11·2	10·2	8·6	13·8	12·4	9·8	8·4	11·5	11·3	8·8	8·2	15·8	15·5	13·8	10·8	15·3	10·5	8·2	7·5	13·3	12·2	10·2	8·7
	20	23·2	18·8	19·0	15·9	23·0	18·3	18·0	14·8	21·8	20·1	17·8	17·3	24·5	26·0	23·5	22·0	23·8	18·9	15·5	15·3	23·3	20·4	18·8	17·1
	30	30·0	29·5	29·1	26·4	35·3	34·8	28·0	25·3	31·3	29·3	27·0	28·3	35·8	34·5	34·8	34·5	35·7	28·4	24·5	24·7	33·7	31·3	28·7	27·8
	40	36·6	36·8	37·0	31·2	44·1	36·0	36·5	26·8	41·5	39·9	36·0	32·0	52·0	46·5	43·8	42·0	40·5	33·3	32·3	28·4	42·9	38·5	37·1	32·1

Weight of wool on underslung worker per unit rate of feed — $\frac{\text{grams}}{\text{lb /hr.}}$

	Fancy	F.1				F 2				F 3				F 4				F.5				Average m_5			
	Speed r p m / Rate of feed lb /hr.	342	358	384	406	342	358	384	406	342	358	384	406	342	358	384	406	342	358	384	406	342	358	384	406
B	10	10·9	11·2	10·2	8·6	13·8	12·4	9·8	8·4	11·5	11·3	8·8	8·2	15·8	15·5	13·8	10·8	15·3	10·5	8·2	7·5	13·3	12·2	10·2	8·7
	20	11·6	9·4	9·5	8·0	11·5	9·2	9·0	7·4	10·9	10·1	8·9	8·7	12·3	13·0	11·8	11·0	11·9	9·5	7·8	7·7	11·7	10·2	9·4	8·6
	30	10·0	9·8	9·7	8·8	11·8	11·6	9·3	8·4	10·4	9·8	9·0	9·4	11·9	11·5	11·6	11·5	11·9	9·5	8·2	8·2	11·2	10·4	9·6	9·3
	40	9·2	9·2	9·3	7·8	11·0	9·0	9·1	6·7	10·4	10·0	9·0	8·0	13·0	11·6	10·9	10·5	10·1	8·3	8·1	7·1	10·7	9·6	9·3	8·0

Experiment IV

The effect of fancy speed and rate of feed on the clearing efficiency of five different fancies

The results just described were obtained with one fancy only and it was thought that they ought to be confirmed with other types of fancy. Five fancies were accordingly taken and the following tests done with each in turn.

A batch of Kerry lambs wool was given the same treatment as before on the Garnett breast and first two swifts of another machine. The lap from the Tatham feed was cut into 60 in lengths and fed to the unit card.

The conditions of operation were as follows:—

Swift speed 84 r.p m.
Workers' speed 4·5 r.p m.
Doffer speed 10 r.p.m.
Fancy speeds 342, 358, 384 and 406 r.p.m.
Rates of feed 10, 20, 30 and 40 lb./hr.

The settings of workers to swift and doffer to swift were kept constant throughout the whole series of tests

In addition, in view of the findings of Test 2 a test was done at 40 lb./hr. rate of feed, at each fancy speed, but with the doffer running at 4·5 r.p m. Thus in all 20 tests were made on each fancy, measuring m_5—the amount of wool carried by the underslung worker.

All fancies were set to the swift as far as possible exactly alike by chalking the swift and using this to gauge the equality of the area of contact of each fancy and the swift. All fancies were the same diameter and they were of the following types:—

F.1 A normal type with fillet clothing and a straight wire.
F.2 With fillet clothing and a strong wire. The strongest fancy.
F.3 A sheet fancy with straight wire
F 4 A fancy with wire of sickle bend form.
F.5 With fillet clothing straight wire with a very open zig-zag setting.

The results which were obtained in this test are given in Tables VIII and IX.

It will be noted that the results set out in Table VIII refer to running conditions in which the swift is not likely to be heavily loaded as the doffer was running at the highest available speed, *i.e.* 10 r.p.m In the top half of the Table, A, the weights of wool found on the underslung worker are given, and in the lower half, B, these results are reduced to the amount of wool on the underslung worker per unit rate of feed into the machine. At the bottom right hand corner of the table the average results for the five fancies are worked out.

Table IX

m_5—weight of wool on underslung worker—Effect of fancy speed at slow doffer speed—4 5 r p m —and high rate of feed—40 lb./hr.

Fancy	Fancy speed r.p.m			
	342	358	384	406
F 1	55 8	59 9	60 5	55·0
F.2	54 0	50 8	54 5	54 8
F 3	57·0	56 2	53 7	56 7
F 4	49 0	48·2	47 0	46 5
F 5	52 3	50·7	46·5	45 3
Average ...	53·6	53 2	52 4	51·7

It will be seen for each fancy for every rate of feed adopted the effect of increasing fancy speed was to render its action more efficient because less wool was found on the underslung worker as the fancy speed was increased. As the rate of feed increased, however, the benefit obtained from increased fancy speed diminished For example at 10 lb./hr. rate of feed (on the average values for the 5 fancies), the effect of increasing the fancy speed from 342 to 406 r.p.m. can be estimated by the ratio of 13·3 to 8·7, *i.e.* 1·53 At 20 lb./hr. the corresponding ratio is 1·36, at 30 lb./hr., 1 20, and at 40 lb./hr. 1·34.

These results are in accordance with those found in Experiment II, under the conditions of a quickly running doffer.

Secondly we may note the effect of increasing the rate of feed. In general in all cases the effect of increasing the rate of feed was to decrease the amount of wool on the underslung worker per unit rate of feed into the machine Considering the average results for all 5 fancies it can be shown, however, that as the fancy speed increased there was less benefit from the increased rate of production; for example at a fancy speed of 342 r.p m the ratio of the unit amounts of wool on the worker 13·3/10·7=1·24; at 358 r p.m.=12·2/9·6=1·27; at 384 r.p.m =10·2/9·3=1·10 and at 406 r.p.m.=8·7/8·0=1·09. These results are also in accordance with the conclusions of Experiment II

We turn now to the results shown in Table IX, data collected from these 5 fancies when conditions were such as to place a heavy load on the swift. These were conditions of a high rate of feed and a slow doffer.

Under conditions of light swift loading we have just seen that as fancy speed is increased the amount of wool on the underslung worker decreases, but under these new conditions of heavy loading, it can be seen that the benefit of increased fancy speed is negligible. This is also in accordance with the conclusions of Experiment II.

CONCLUSION

The four experiments described show by a new experimental technique how the efficiency of the action which clears the wool from a card swift is affected by doffer-swift setting, doffer speed, fancy speed and rate of feed. The conclusions stated at the end of Experiment II will not be repeated, but it may be remarked that the truth of these conclusions has been confirmed with several wools and 5 fancies all of which exhibit the same behaviour.

ACKNOWLEDGEMENTS

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REFERENCE

[1] Martindale, J. G. *J. Text. Inst*, 1945, 36, T213

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51—A NEW APPARATUS FOR MEASURING THE DENSITY OF FIBRES

By S. H. MHATRE and J. M. PRESTON

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INTRODUCTION

A method has been devised for measuring the densities of fibres, from which their sorption of solutes can be calculated. Density determinations enable the quantities of solute sorbed to be determined more accurately than can be done by ordinary analytical methods. A float method was adopted for measuring density. Suspended floats have been used by various workers, but there is always the uncertainty introduced by the correction factor for the surface tension pull on the suspending wire. To make this as small as possible, very fine wire has been used. To reduce the surface tension pull to values of the order of 1 milligram, wire as fine as 50 S W.G must be used. Such fine wire is very fragile and can be used only with very light floats. To avoid this difficulty altogether it was decided to use a totally immersed float

When using totally immersed floats one method of controlling the float so as to balance the buoyancy of the liquid is by the "Cartesian diver" principle. In this method the buoyancy of the float is varied by varying the volume of the float. This can be done if the float is made with a thin and deformable panel in it. When the external hydrostatic pressure is increased the float diminishes in volume and its buoyancy is correspondingly reduced. In any measurement the hydrostatic pressure is steadily increased by applying air pressure to the vessel containing the float till the float just sinks. The float is calibrated in a series of solutions of known densities by determining the air pressures required for sinking the float in each case. In use, the method presented several difficulties, one of which was the difficulty of knowing the changes of density introduced by the changes in amount of air dissolved at different pressures Another difficulty was the fragility of the floats. The thin deformable panel in the head of the float was very easily fractured. Because of these difficulties the method was abandoned and an electromagnetic method was adopted.

Previously Lamb and Lee[1] and Bishop[2] had used electromagnetic methods. The former workers used a large float of 250 c.c. and a very large volume of liquid, about 4 litres, and claimed a very high accuracy of measurement. Bishop devised a routine method of comparatively low accuracy. For the present work an accuracy lying between the accuracies of these two methods was required. It was necessary to use far smaller volumes of solution than were used in the Lamb and Lee method, and it was also desired to use the method for measuring the densities of fibres.

APPARATUS AND METHOD

The apparatus finally designed used a float *F* of about 5 c.c. capacity in a tube *D* holding about 150 c c. of liquid, as sketched in Fig. 1. The density tube is completely filled with liquid in a special apparatus described later The density tube containing the float is mounted co-axially inside a large tube, *H*, and held in position by brass "spiders" *B*, *B* The outer tube *H* is in effect a thermostat. Water is circulated through this by a Stuart No 10 centrifugal pump. The circuit of the water circulating system contains a large vessel of 5 litres capacity filled with a mixture of crushed ice and water which is kept continuously stirred by an electric motor and stirrer. In these circumstances the temperature in *H* is kept constant to within ±0·005° C. The tem-

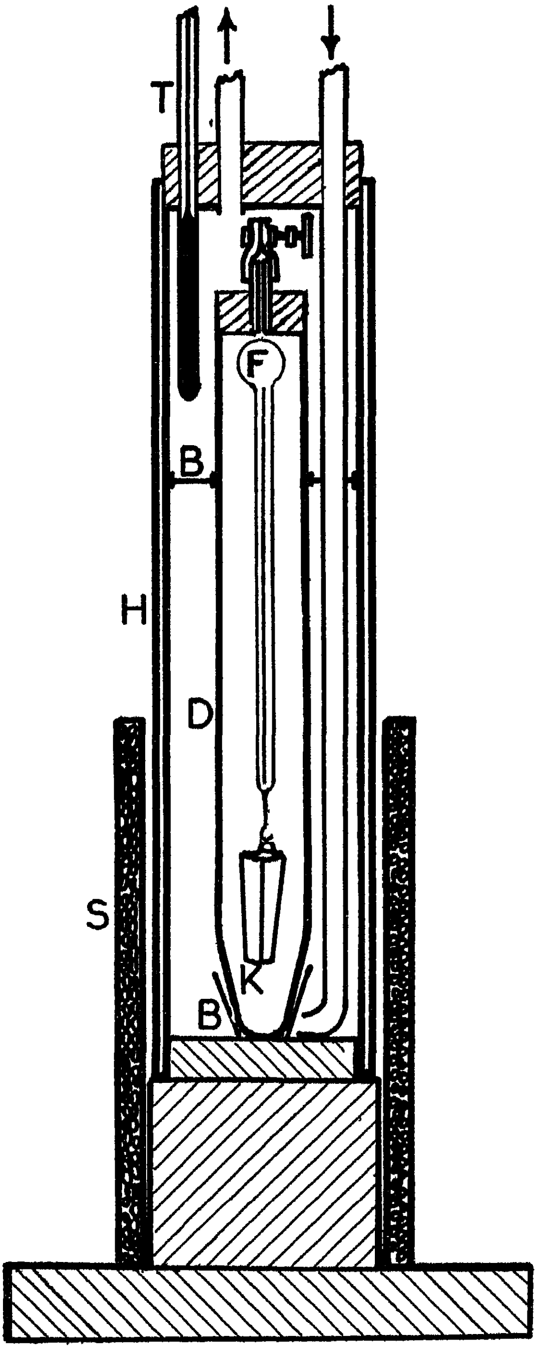

Fig. 1

perature is observed on an accurate thermometer, *T*, graduated in 0·01° C. The operating temperature is found to be 0·30° C. In later work a Townson and Mercer type S127 thermostat has been used at a temperature of 30° C. and water from this is by-passed through the tube *H*. This gives a similar constancy of temperature.

The outer tube *H*, is mounted co-axially inside a solenoid, *S* The design of the solenoid was carefully considered with a view to obtaining as uniform a field as possible. Data in the literature indicated that the length of the solenoid should be at least twice its diameter. The pull on a long armature should then be uniform over more than a third of the depth of penetration of the armature into the solenoid. A solenoid was wound on a brass tubular former of 9·5 cm. diameter and 22 cm. length. 1,000 turns of 17 S.W.G. copper wire were wound on the former. This had a resistance of about 6·5 ohms. The float contained a 16·5 cm. length of soft iron wire of 0·23 mm. diameter. The pull on the float produced by a current in the solenoid was measured when the float was at different levels in respect of the penetration of the armature into the solenoid. The level of the float was obsrved with a cathetometer and the pull on the float was measured by the current required to permit the float just to rise very slowly when the armature was at different levels The results are shown in Fig. 2. It will be seen that there is a range of uniform pull over about 2 or 3 cm. This is very convenient because it means that when making a measurement the exact position of the float is immaterial provided the armature lies within this range. The density tube, *D*, is fixed at a convenient level so that the float lies within this range when pulled down to the bottom of the tube.

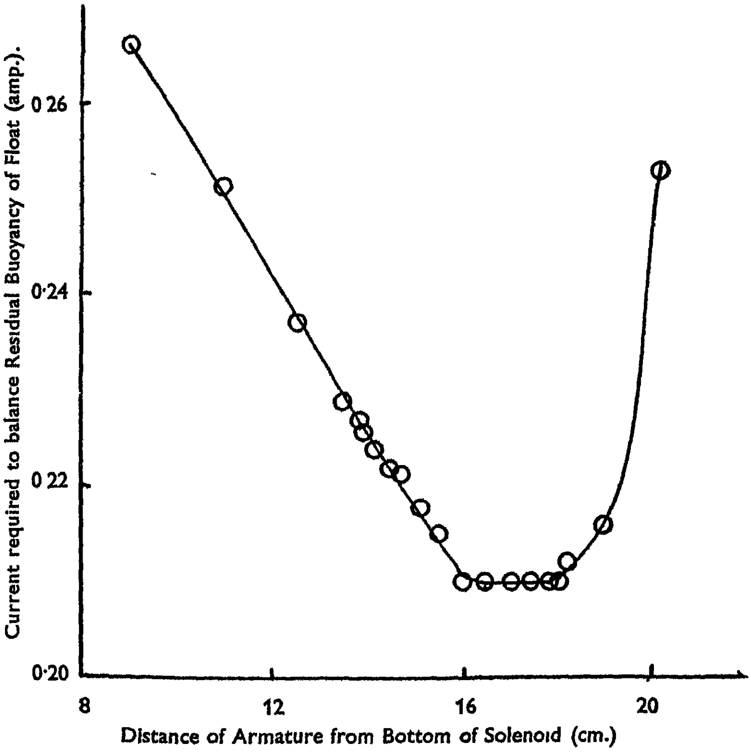

Fig. 2

To make a measurement the float is pulled down by sending a current of 1·2 amp. through the solenoid. This has the effect of centring the float since the density tube *D* is conical at the bottom. The current is then slowly reduced till the float just rises. The current through the solenoid is now measured, which from the calibration curve gives the pull on the float.

The possibility of hysteresis in the iron of the armature was considered as a disturbing factor, but it was found that provided the same routine was followed the results were well reproducible

The routine of measurement was to pull down the float with a current of 1·2 amp. and then slowly to reduce the current as described. It was found that there was a linear relation between the solenoid current and the armature pull as shown in Table I below

Table I

Calibration of the current in the solenoid and the pull on the float

Temperature of water.. 0 30°C .
Density of water ... . 0 99989 g./c c
Density of platinum . . . 21·45 g /c c

Platinum weights after correction for buoyancy in water mg.	Current required to balance float and weights milliamperes	Current equivalent to the weights added milliamperes	mg per milliampere
0 00	916	—	—
4·26	718	198	0 0216
6 93	593	323	0 0125
9 95	453	463	0·0215
12 94	314	602	0·0215
16 75	137	779	0 0215

The current through the solenoid was used only to produce pulls on the float at the most of 20 milligrams and by a current of 1 amp. If larger pulls were required they were obtained by a combination of platinum weights hung from the float and electromagnetic pulls given by the solenoid. In practice this has meant that the first two decimal places of density were obtained with the weights and the last three places by the current through the solenoid. Currents of less than 137 milliamperes were not used and therefore it is possible that the relation was not linear for the smallest currents.

The earlier workers had recommended using a soft iron armature, and an iron wire which was believed to be soft was used at first. Consideration of the factors involved, however, showed that soft iron could not give a linear relation for the smallest currents because of the shape of the hysteresis loop However, a linear relation was observed with the lowest current used This is shown by the data of Table I. It is possible that the heat treatment that had been used for straightening the wire may have hardened it. As the essential condition for getting a linear relation between solenoid current and armature pull is that the armature maintains a constant intensity of magnetization, it appears preferable to use a metal for the armature which would have better retentive properties. As magnetic materials of the type of Alnico were not available in the desired form of thin wire the best that could be used was an ordinary hard steel wire. A fresh float was therefore constructed using a steel wire of 0·25 mm. diam and 16·5 cm long The relation between current and the pull on the armature was re-determined. It was again found to be linear within the experimental error over the range tested and this confirmed the view that what was required was a permanent magnet for the armature In view of this the hard steel wire armature is being used for all further work.

The accuracy of the method used is believed to be 2 parts in 100,000 with a 5 c.c. float In making calculations of the density of a solution the weight of the float in air enters into the calculation twice, once in the determination of its volume from its weights in air and water and again whilst determining the density of the liquid under measurement. Because of this its absolute value is less important than appears at first sight. Thus if the allowance for the buoyancy of the float when weighed in air is omitted it introduces a small error. This can be seen as follows:

Let w = weight of float in air.
w_1 = weight of platinum weights used with water
w_2 = weight of platinum weights used with solution under test.
x_1 = pull on armature to balance in water.
x_2 = pull on armature to balance in solution
σ_1 = density of water.
σ_2 = density of solution.
σ_3 = density of platinum.

The volume of float + platinum weights used with water

$$= \frac{w+w_1+x_1}{\sigma_1}$$

$$\text{Volume of float} = \frac{w+w_1+x_1}{\sigma_1} - \frac{w_1}{\sigma_3} = A$$

When the upward and downward forces are balanced

$$\sigma_2\left(A+\frac{w_2}{3}\right) = w+w_2+x_2$$

$$\sigma_2 = \frac{w+w_2+x_2}{A+\dfrac{w_2}{\sigma_3}} = \frac{w+w_2+x_2}{\dfrac{w+w_1+x_1}{\sigma_1} - \dfrac{w_1}{\sigma_3} + \dfrac{w_2}{\sigma_3}}$$

$$= \frac{w+w_2+x_2}{\dfrac{w+w_1+x_1}{\sigma_1} + \dfrac{(w_2-w_1)}{\sigma_3}}$$

The buoyancy of the float in air introduces an error in the weight of the float of $-6\ 45\times 0\ 00107 = -0\cdot00690$ g. and an error in the platinum weights of $+w_1$ (or w_2) $\times 0\cdot00009$ gm. Since w_1 and w_2 are never greater than 1 g, the greatest correction for the buoyancy of the platinum weights is $+0\cdot00009$ g. Because the term enters both into the numerator and the denominator of the above expression, a small error in w does not affect the value of σ_2 very much. An example will make this clear

$w = 6\cdot4571$ g.
$w_1 = 0\cdot01958$ g
$x_1 = 0\cdot00480$ g.
$w_2 = 0\ 11929$ g.
$x_2 = 0\cdot02015$ g
$\sigma_1 = 0\cdot99988$ g./c.c
$\sigma_3 = 21\ 45$ g./c.c.

$$\text{Thus}\quad \sigma_2 = \frac{6\cdot4571+0\cdot11929+0\cdot02015}{\dfrac{6\cdot4571+0\cdot01958+0\cdot00480}{0\cdot99988} + \dfrac{0\cdot11929-0\cdot01958}{21\cdot45}}$$

$= 1\cdot01690$ g./c c.

If the correction for the buoyancy in air is made and all the weights are referred to *vacuo*

$w = 6\cdot4631$ g.
$w_1 = 0\cdot01958$ g.
$w_2 = 0\cdot11928$ g

x_1 and x_2 are the same as before and the density after applying these corrections is given by

$$\sigma_2 = \frac{6\cdot4631+0\cdot11928+0\cdot02015}{\dfrac{6\cdot4631+0\cdot01958+0\cdot00480}{0\cdot99988}+\dfrac{0\cdot11928-0\cdot01958}{21\cdot45}}$$

$$=1\cdot01689 \text{ g./c.c.}$$

Thus the buoyancy correction does not introduce any serious error in this case For solutions of higher density a greater error is caused by the omission of the buoyancy correction. In all the data given, however, correction was made for the buoyancies in air.

A variation of the temperature of the liquid in the density tube if it has a thermal expansion similar to that of water is less important near the freezing point than at higher temperatures. Thus the change in density for a variation of 0·1° C. at 0·3° C. is 0·6 in 100,000, whilst at 30° C. it is five times as great, so that a temperature range ±0·1° C. is sufficient at 0·3° C., but at 30° C. the temperature variation should not exceed ±0·02° C. The temperature variation in both cases was less than this

Electrical Circuit

The electrical circuit used is shown in Fig. 3. The diagram shows that there are in effect two electrical circuits. The solenoid circuit is made up of the accumulators, *B*, the current from which is controlled by the variable resistance R_1, and indicated approximately by the ammeter, *A*, in series with the solenoid, *S*, and a standard 1 ohm resistance, R_2. The control of the float is obtained by varying R_1. The current flowing through the solenoid circuit is indicated precisely by the potential drop across R_2. This is measured with the help of the potentiometer circuit.

Verification of the Accuracy of the Apparatus

A check upon the accuracy of the apparatus was obtained by measuring the density of a solution of Analar sodium chloride of known strength. Allowance was made for the buoyancy of the platinum weights in the liquid being measured These were all made from the same lot of wire and the density was taken as 21·45 g./c.c. An interpolated value of the density of the solution of the concentration used was obtained from the data given in the literature [4] The values are given below:

Sodium chloride concentration	6·4796 g /100 g. solution at 0·3° C.
Density-Interpolated value[4]	1·04943 g./c.c.
Density-Densitometer value	1·04941 g./c.c

FIBRE DENSITIES

The density of fibres in water can be determined by finding the weight of the fibres in air and in water. This gives the volume of the water displaced by the fibres and their density can be calculated The weight of the fibres in water can easily be determined with the help of the densitometer

Air dry fibres about 1 g were packed in a small conical glass basket weighing about 1 g After packing the dry fibres in the basket *K*, in Fig 1, a yarn of the same fibres was wrapped round the basket a few times to prevent any loose ends from protruding and touching the side of the density tube The float, together with the empty basket, was weighed in air, and the weight in water was determined with the densitometer.

The packed basket and the control samples of the same fibres were conditioned for a week at 64 per cent. R.H. The moisture content of the control samples was determined by weighing and drying in an oven at

110° C. to constant weight. The moisture content of the fibres packed in the glass basket was taken to be the same and thus the amount of oven dry cellulose present was known without the complication which would have been introduced by drying the sample itself

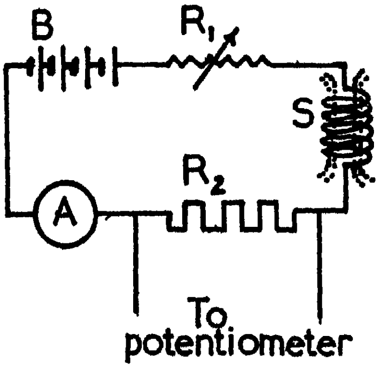

Fig 3

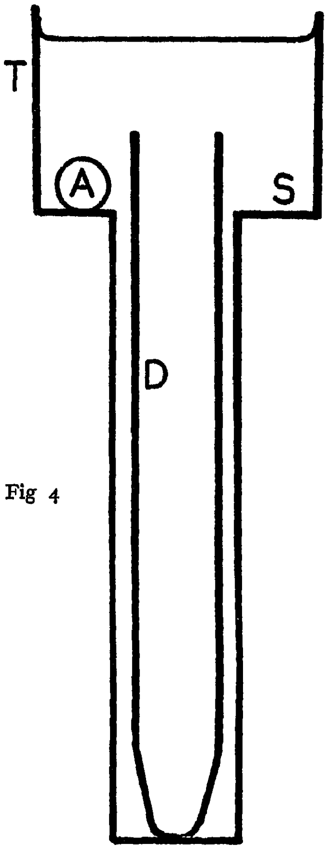

Fig 4

The fibre sample was de-aerated in a manner similar to Herman's procedure[5] by boiling in water for 30 minutes and allowing to remain submerged at room temperature for 24 hours. The basket and fibres were transferred to the density tube without being taken out of water. The procedure was to transfer the basket and fibres to a small tube full of water, keeping them submerged. The small tube, *A*, was now transferred to the shelf *S* of a special stainless steel trough *T*, shown in Fig. 4. The trough had previously been filled with boiled out water after the density tube, *D*, had been packed in it. Then the basket containing the fibres was hooked on to the bottom of the float and transferred whilst still submerged from the shelf of the steel trough and lowered into the density tube. Any platinum weights required were attached at the same time.

The densitometer tube was stoppered with a rubber stopper through which passed a glass capillary tubing carrying a short length of rubber tube together with a screw clip. When the stopper was being fitted in the tube, the screw clip was left open, and this allowed water to escape. Afterwards the clip was closed. The filled density tube was placed in the thermostat as shown in Fig. 2. About 1½ hours were allowed for temperature equilibrium to be attained and the balancing current was determined as before.

The calculation of the density is made as follows:

Determination of the Volume of the Float and Basket

Weight of the float	4 1622 g.
,, ,, ,, basket	1·1550 g
,, ,, ,, platinum weights added	0·71446 g.
Pull due to the current in the solenoid	0·00628 g.
Total weight and pull of the system	6·03794 g.
Volume of the system $=\frac{6\cdot03794}{0\cdot99988}=$	6·03866 c.c.
,, ,, ,, platinum weights	0·03331 c c.
,, ,, ,, float and basket	6·00535 c c.

Determination of the Density of Viscose in Water

Weight of the basket and fibres conditioned at 64 per cent. R.H	2·6265 g.
,, ,, ,, fibres conditioned at 64 per cent. R.H.	1 4715 g.
Moisture content from separate determination	12·04 p.c
Weight of the oven-dry fibres	1·2941 g.
,, ,, ,, platinum weights added	0·20043 g.
Pull due to the current in the solenoid	0 00353 g.
Total weight and pull of the system	6 81524 g
Volume of the system $=\frac{6\cdot81524}{0\cdot99988}=$	6·81605 c c.
Volume of the float, basket and platinum	6·01470 c c
,, ,, ,, fibres	0·80135 c.c.
Density of the fibres	.$1\cdot6149_0$ g./c.c.

This determination was done in quadruplicate with the results shown below:

$$\left.\begin{array}{l}1\cdot6149_0\\1\cdot6150_0\\1\cdot6149_4\\1\cdot6150_6\end{array}\right\}\text{Mean } 1\cdot6149_7$$

It will be seen that these values agree to ±0·7 in the fifth decimal place. Better agreement could not be expected since the dry fibres were weighed to the fourth decimal place only. Comparative values from the literature for "normal" viscose rayon fibres are·

1·6084 Davidson.[7] 1·6143–1·6203 Hermans.[6]

The results obtained with the new method are in Hermans' range, but no exact comparison should be attempted since different fibres were used in all cases, and it is known that the density in water varies with the degree of crystallinity and possibly it also varies with other factors as well.

When examining the calculation of density given above it will be noted that the weights of the basket and float are given to the fourth decimal place only This does not preclude results being obtained to the fifth decimal place if the fibres are weighed to this accuracy when dry. The reason for this is that the weights and volumes of the float and basket enter into the calculation twice in the form of a difference and any errors in their measured values are automatically annulled

REFERENCES

[1] Lamb and Lee *J A C.S* , 1913, 35, 1666.
[2] Bishop *J. Inst Brewing*, 1934, 40, 92
[3] Pendler and Delmar *Electrical Engineer's Handbook.* New York, 1936 Section 4, p 29
[4] International Critical Tables, Vol. III, p. 79
[5] Hermans Contributions to the Physics of Cellulose Fibres. Elsevier. Amsterdam, 1946 p 213
[6] Hermans *Ibid.*, p 95
[7] Davidson *J. Text Inst.*, 1927, 18, T 175.

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52—THE UREA-PHOSPHORIC ACID METHOD OF FLAMEPROOFING TEXTILES

By F. V. Davis, J. Findlay and E. Rogers

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SUMMARY

It has been confirmed that a flame-resisting property, capable of withstanding mild laundering, can be imparted to cellulosic fabrics by treatment with urea and phosphoric acid followed by heating The chemistry of the process is investigated.

I. INTRODUCTION

The Bancroft Co., of U S.A., was granted a patent in 1945 and subsequently a series of patents relating to a method claimed to impart to cellulosic fabrics a flame-resisting property capable of withstanding water and mild laundering without unduly impairing strength or other properties The obvious interest of such a method to the Services prompted an investigation of this claim which is reported here together with some observations on the chemistry of the process.

According to the earliest Bancroft patent, a flameproof finish capable of resisting washing with hot water is imparted to cotton cloth by applying a mixture of 1-4 parts of urea and 1 part of phosphoric acid to the fabric by padding, drying the impregnated cloth, and then "curing" it by heating at temperatures between 125° and 175° C. The amount of total solids added to the fabric at the padding stage is stated to be about 68 per cent. of the initial weight of the cloth. This treatment is said to involve a loss in strength of 15 per cent. under the best conditions. Mention is made of the fact that less tendering of the fabric occurs if the urea-acid mixture is pre-heated before application to the fabric. In a subsequent patent specification a mixture of 2 parts of urea, and 1 part of 75 per cent. phosphoric acid was used which was heated to 140°-170° C., cooled, diluted, rendered slightly alkaline with ammonia, and treated by addition of an aldehyde, *e g* formaldehyde. The remaining patents of the series deal with relatively minor modifications, more especially with the partial substitution of the urea by another organic base.

Preliminary experiments substantiated in a qualitative way the claims made for the patented process and showed that no flameproofing effect followed if the temperature of curing was below 130° C. The upper practical temperature limit was about 175° C., above this temperature scorching occurs.

Following these preliminary trials a systematic investigation into the effects of the several variables on the efficiency of the process was carried out, and some consideration was given to the elucidation of the chemistry involved. These experiments are described in detail below

Between the conclusion of this work and its publication in the present form, a letter appeared in the technical press[9] which discusses earlier ideas and confirms some of our findings. Also it has been proposed to put the strong ion exchange behaviour of phosphorylated cellulose to practical use.[10]

II. DISCUSSION

The series of trials recorded in Table I showed that whilst most of the solid matter added at the padding stage had been removed by the washing treatment some phosphorus and nitrogen were fixed by the cellulose, and that the efficiency of the flameproofing was proportional to the amount of phosphorus fixed At the same time, the loss in strength increased with the amount of phosphorus bound, so that it would, in practice, be a question of balancing acceptable loss in strength against adequate fixation of phosphorus. For complete flameproofing, by which is meant inability of the fabric to propagate flame at all after withdrawal of the source of ignition, a minimum of about 3 per cent phosphorus on the weight of cloth seemed necessary, and with this amount of phosphorus a loss in strength of about 20 per cent was found.

It did appear that pre-heating the urea and acid mixture before application to the cloth reduced tendering, this is not surprising, as a simple mixture of the urea and acid had a *pH* value of 1·8, whereas after heating the substances together the *pH* value rose to 5-6.

Further series of experimental trials, using the formaldehyde modification of the process, studied the effect of variations in curing conditions on fixation of phosphorus and loss in strength (Table II).

These trials confirmed the view that a completely flameproof finish could be obtained by adjusting curing conditions so that 3 per cent. or more of phosphorus was fixed by the fabric, and that, for this phosphorus content, a loss in strength of about 20 per cent. was normal. The time of cure necessary was found to be between 1 and 2 hours at 130° C., and about 5 minutes at 175° C. Obviously treatment at 130° C. would be very slow for commercial work, but if the highest temperature-range is used, very close control of both temperature and time will be necessary if under-cure (and hence poor flameproofing efficiency) on the one hand, and over-cure (and hence undue tendering and perhaps scorching) on the other hand, are to be avoided.

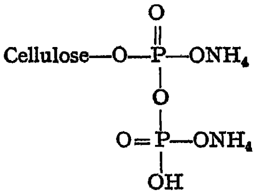
At the commencement of this work, the mechanism of the process was obscure, and in fact, not even the initial reaction between urea and phosphoric acid appeared to be understood The patentees claimed that the urea neutralised the acid and acted as a buffer, but this is clearly an over simplification, as urea does not form neutral salts by substitution, but acid salts by addition.

Our experiments indicate that di-ammonium pyrophosphate is formed and that this salt, in presence of urea, is the effective fireproofing agent.

Fabric from which the nitrogen had been removed by a caustic alkali boil was not flameproof despite its phosphorus content; it became flameproof on treatment with acid, and lost its flameproof property again when treated with a metal salt It would seem that a compound, probably an ester, with acidic properties is formed, the acid ester and its ammonium salt confer fireproof properties, whereas the salts of sodium or other metals do not.

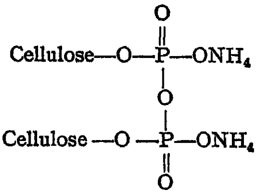
The behaviour with methylene blue and with cuprammonium solution is consistent with the formation of a cellulose ester. Confirmation of ester formation, and evidence as to whether the ester is a pyrophosphate or an orthophosphate, can be obtained by calculating the ammonium and phosphorus fixed in terms of the two esters and comparing the results with the observed increase in weight. The ratios between phosphorus and ammonia, phosphorus and lead in the case of fabrics treated with lead salts, phosphorus and sodium in the case of fabrics treated with caustic soda, will differ for orthophosphate or pyrophosphate formation, and so may yield evidence as to which ester is formed

The mean gain in weight is close to that calculated from the observed phosphorus content on the assumption of orthophosphate formation (Tables VII and VIII), but the scatter of individual tests is rather large. The atomic ratio of phosphorus to ammonia is 1:0·94 (Table XI) and 1:0·85 (Table VII); the atomic ratio of phosphorus to lead is 1:1·05 (Table IX) and 1:1·07 (Table X), whilst the atomic ratio of phosphorus to sodium is 1.1·85 (Table XI). If the ester is a pyrophosphate it will presumably be either



$$\text{Cellulose}-O-P(=O)(ONH_4)-O-P(=O)(ONH_4)-OH$$

or



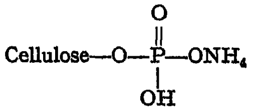
$$\text{Cellulose}-O-P(=O)(ONH_4)-O-P(=O)(ONH_4)-O-\text{Cellulose}$$

Neither of the above formulæ, however, would permit of the formation of compounds containing the following:—

(*a*) Phosphorus to lead ratio of 1:1 (Tables IX and X).

(*b*) Phosphorus to sodium ratio 1.2 (Table XI)

It seems, therefore, that whilst the ester first formed may be a pyrophosphate the final product present on the fabric after washing must be the orthophosphate



$$\text{Cellulose}-O-P(=O)(ONH_4)-OH$$

since this would explain the formation of the metallic compounds mentioned above.

In contrast to the literature on nitration and organic esterification, the published work on phosphorylation of cellulose is very scanty and most of it consists of patent claims, primarily for production of bases for lacquer.[1-7] Birtwell, Clibbens and Geake[8] studied the hydrocellulose formation when phosphoric acid was dried into cotton cellulose at temperatures up to 130° C. for 2 hours. They noted high methylene blue absorption both at *pH* 7·0 and *pH* 2·7, and found evidence for fixation of a small amount of phosphorus (up to about 0·1 per cent.) which was not removed even by caustic alkali Their products were highly degraded, and in fact hydrocellulose formation appears to be always the main result of treating cellulose with phosphoric acid.

It is suggested that the excess of urea, being liquid at the temperature of curing, may act as a solvent or medium assisting esterification.

The formation of a pyrophosphate from an orthophosphate at 175° C is unexpected, as the transition temperature for orthophosphates heated alone is normally given as 225° C

III. EXPERIMENTAL

The results of the experiments described below are recorded in the Appendix (Tables I-XI and the figure) Fabrics in the tests were conditioned at room temperature unless otherwise stated.

1. Padding and Curing Procedure

For padding, a laboratory mangle was constructed which could reduce the retention of absorbed liquor to 85 per cent. of the fabric weight, although in the experiments a liquor retention of 100 per cent. was normally used. The width of fabric taken by the mangle was 20 inches.

For curing, an electric heater was constructed in which a hot air current rose by convection from two heater spirals, one of 1½ kilowatt and the other of ½ kilowatt. The latter was wired in series with a Sunvic control, so that any desired temperature between 125° C and 175° C could be maintained within 1° C. The cloth was stretched on a rectangular frame carrying metal pins about 0·5 inches apart; this frame could be slid into the upper part of the heater

Light twill cotton fabric was used throughout the experiments and being bleached did not present any processing difficulties prior to impregnation After padding, the cloth patterns were air-dried at laboratory temperature, and then mounted on the frame which was slid into the dryer, previously brought up to the desired curing temperature. After curing, the cloth patterns were washed in water to remove unfixed soluble matter, rinsed and dried.

2. Effect of Variations in Impregnant and Cure on Fixation and Loss in Strength

Padding liquors were prepared either by mixing the desired amounts of urea and 75 per cent. phosphoric acid with water, or by heating the urea and phosphoric acid together at 100° C for 3 hours, and then adding the requisite amount of water to dissolve the product at room temperature. The former solutions are referred to as "Acid Liquors", and the latter as "Neutral Liquors". The liquors used were as follows:

Acid Liquors: (i) 2·7 g of urea and 1 g of phosphoric acid dissolved in 4·4 ml. of water;
(ii) 1 g. of urea and 1 g. of phosphoric acid dissolved in 1·7 ml. of water;

Neutral Liquors: (i) 1 g. of urea and 1 g of phosphoric acid dissolved in 1·7 ml. of water;
(ii) 1 g. of urea and 1 g. of phosphoric acid dissolved in 1·35 ml. of water.

Portions of fabric were padded in suitable volumes of each of the four liquors to give a liquor retention of approximately 100 per cent on the original weight of the fabric For each of the four types of impregnant, three pieces of fabric were cured at 150° C. for different periods of time

Loss in strength, flameproofing, phosphorus and total nitrogen contents were determined on cured patterns which had been washed in water at 70° C., rinsed, dried and conditioned. The results are given in Table I.

3. Effect of Variations in Cure on Fixation and Loss in Strength of Fabrics Impregnated with Liquor treated with Formaldehyde

The impregnating liquor was prepared by heating 200 g of urea and 100 g. of 75 per cent. phosphoric acid to 175° C., at which point heating was discontinued and the mixture allowed to cool Before the mixture could solidify successive additions of 100 ml. of water, 16 ml. of ammonia (0 880) and 45 ml of formaldehyde (40 per cent) were made.

The fabrics were impregnated and the expression of liquor was adjusted to leave 100 per cent by weight of liquor on the weight of the fabric.

After drying, the fabrics were cured at 130° C. for 30, 60, and 120 minutes, at 137° C. for 30 and 60 minutes, at 145° C for 30 minutes; at 160° C for 15 minutes, and at 175° C. for 10 minutes

All the cured patterns were washed in water at 55° C. for 15 minutes, then rinsed in cold water and dried. On the washed fabrics total nitrogen, phosphorus and loss in strength were determined. The results are given in Table II

The loss in strength is greatest at high curing temperatures. Low temperature curing is slow.

4. Effect of Washing Treatments on Retention of Nitrogen and Phosphorus of Fabrics treated with Liquor modified by means of Formaldehyde. Series I.

The liquor used was similar to that employed in the preceding trials, and the impregnation was also on the same lines. The dried fabrics were cured at 145° C. for 20 minutes, and at 175° C. for 8 minutes. One portion of fabric from each cure was washed in water at 55° C. for 15 minutes, followed by a rinse in cold water. When dried, these samples were tested for phosphorus and total nitrogen content. A second portion from each of the cured fabrics was washed in a solution containing 0·5 per cent soap and 0·2 per cent. sodium carbonate at 80° C. for 30 minutes. The comparative results are shown in Table III.

There is a marked drop in the nitrogen content due to the alkaline scouring treatment. The apparent increase in strength of the fabric treated with soap is probably due in large measure to shrinkage.

5. Effect of Washing Treatments on Retention of Nitrogen and Phosphorus. Series II

A fabric impregnated with liquor treated with formaldehyde was cured, and subjected to washing treatments of various degrees of severity, and the total nitrogen and phosphorus contents were determined. Nitrogen present as the ammonium radicle was determined by distilling the fabric with sodium carbonate solution. The actual treatments used were:—

(*a*) Cured only, no after rinse.
(*b*) Washed-off in water at 70° C. for 15 minutes, rinsed in cold water, dried.
(*c*) Scoured in a solution containing 0·5 per cent. soap, and 0·2 per cent. anhydrous sodium carbonate in a reversing wash-wheel at 70° C. for 30 minutes, rinsed in water at 40° C., rinsed off in cold water, and dried.
(*d*) Washed as in (*b*) above six times in succession, with intermediate rinsing and passage through a tight roller nip, then dried.
(*e*) Boiled in 1 per cent. sodium hydroxide solution for 30 minutes, rinsed in water at 70° C. for 5 minutes, rinsed in cold 0·5 per cent. acetic acid, rinsed in water, then dried.
(*f*) Boiled in 1 per cent. barium hydroxide solution for 30 minutes and after-treated as in (*e*) above.

The results are given in Table IV.

Since much of the phosphorus remains after the severe alkali treatment, the phosphorus is obviously firmly bound, whereas the nitrogen is not so firmly bound. The odour of ammonia was apparent on treatment with caustic alkali.

The effect on flameproofing property is recorded in Section 7.

6. Effect of Washing Treatments on Patterns processed by the Patentees

Six patterns processed by the Patentees were tested for resistance to washing by determining phosphorus and total nitrogen contents after various treatments as follows:

(*a*) Fabric as received.
(*b*) Fabric boiled for 30 minutes in distilled water.
(*c*) Fabric washed in wash-wheel for 30 minutes in a solution containing 0·5 per cent. soap and 0·2 per cent. anhydrous sodium carbonate at 70° C.
(*d*) Fabric washed four times successively as in (*c*) above.
(*e*) Fabric washed ten times successively as in (*c*) above.

(*f*) Fabric washed for 30 minutes in wash-wheel as in (*c*) above, but at 94° C.

(*g*) Fabric washed four times successively as in (*f*) above.

(*h*) Fabric boiled in 0·5 per cent. sodium hydroxide solution for 30 minutes.

The results are given in Table V.

The original total nitrogen/phosphorus ratio is high; possibly these fabrics have been processed by one of the later modifications, such as that involving substitution of part of the urea by a stronger organic base like guanidine.

The effect on flameproofing properties is recorded in Section 7.

7. Effect of Alkaline Solutions on Flameproofing

It was observed that flameproof material when subjected to a caustic boil lost its flameproofness, and burned quite freely, although the phosphorus content was little affected When such material was treated with 1 per cent. hydrochloric acid, so as to be definitely acid in reaction, and then washed with distilled water and dried, it again acquired flameproof properties, refusing to propagate flame at all. This acid-treated material on further treatment with 5 per cent. aqueous ammonia and drying retained flameproofness, but the ammonia-treated material on soaking in hot 1 per cent. lead acetate solution, washing and drying became again free burning. It was also found that the original flameproof material, direct from cure and washing off, lost its flameproof qualities on being boiled with 1 per cent. aqueous ferric chloride solution, when it absorbed iron strongly and became khaki in colour.

The samples of fabric processed by the Patentees confirmed these results; the patterns treated as described in Section 6 above with soap and soda detergents and with caustic soda liquor, lost practically no phosphorus, but did definitely lose flameproofing properties; the samples after ten soap-soda scours at 70° C., or four scours at 94° C., showed rates of flame propagation of 6-16 seconds per inch, whilst the material boiled with caustic showed flame propagation of 4-12 seconds per inch On acidification with hydrochloric acid, washing and drying, these materials became again flameproof.

8. Dye Absorption and Reaction with Cuprammonium Reagent

Methylene blue absorption of flameproof material was determined using 1 g of shredded fabric and M/250 methylene blue solution buffered to *p*H 7·0 and to *p*H 2 7. Absorption of colour from the first 20 ml. of solution was practically instantaneous and after 18 hours the following values were obtained (expressed as millimols of methylene blue per 100 g. dry fibre):

	*p*H 2·7	*p*H 7·0
Laboratory-prepared material using "neutral liquor"	32	30
Pattern treated by Patentees	52	52

Cotton fabric rendered flameproof with urea-phosphoric acid impregnant in the laboratory did not absorb acid dyes from an acid dye bath Absorption of the direct colour Chlorazol Sky Blue FF was much less than in the case of untreated cotton controls, and staining by dispersed acetate colours was only slight Shirlastain A gave only an off-white colour resembling that given by Cotopa

When extracted cotton fibres were chopped into short lengths and treated with cuprammonium reagent on a microscope slide, the cuticle was observed to absorb the copper strongly and become deep blue, but it did not tend to dissolve, whilst the inner part of the fibre swelled, giving the well-known "dumb-bell" effect, and swelling continued until the inner part dispersed in the cuprammonium reagent.

9. Reactions of Urea-Phosphoric Acid Mixtures

(i) Mixtures of urea and 75 per cent. phosphoric acid were found to show no reaction at room temperature. When 2·7 g. of urea were mixed with 1 g of 75 per cent. phosphoric acid at room temperature the mixture had an initial *pH* value of about 1·9 in 5 per cent. aqueous solution, and this figure remained unaltered over a period of 4 hours On heating for 4 hours at 40° C. or 70° C. there was no rise in *pH* value above 2·0; but on increasing the temperature to 85-90° C. for 4 hours the *pH* rose to 2·7. Only on heating for about 4 hours at 100° C. did the *pH* of a 5 per cent. solution rise to about 6, and the same result was achieved by heating rapidly up to 175° C. and then allowing to cool.

(ii) 2 g. of urea and 1 g. 75 per cent. orthophosphoric acid were heated together at 175° C. for a lengthy period, and the weight was noted at intervals. The results, which are shown in the figure, indicate that 8-10 hours heating is necessary for the reaction products to approach constant weight.

(iii) 5 g. of 80 per cent. orthophosphoric acid were heated at 175° C. for 8 hours with amounts of urea varying between 24 g. and 1 g. The loss in weight was noted, the phosphorus and the total nitrogen content of the residues were determined, and the yield of ammonia was estimated by treating with 5 per cent. sodium carbonate solution and subsequent distillation. The results are given in Table VI. All the reaction products except the last two were transparent glassy solids. Excluding the two extreme trials, the reaction products all gave almost the same yield of ammonia on distillation with sodium carbonate and the molecular ratio of ammonia to phosphorus was found to be approximately 1 to 1. The nitrogen not removable as ammonia fell as the weight of urea used decreased, and reached zero when 2 g of urea were used with 5 g. of 80 per cent phosphoric acid. This suggested that the reaction product from heating urea-phosphoric acid in the normal proportions of 2 to 1 was a mixture of at least two components, and attempts were accordingly made to separate them. Fractional crystallisation from water succeeded in isolating only a fraction of very low solubility containing 32·1 per cent. nitrogen (Kjeldahl) and only a trace of phosphorus; further concentration and crystallisation was obviously causing hydrolysis and so was abandoned

Separation was effected by adding a small amount of water to the urea-phosphoric acid reaction product (Trial No. 5, Table VI) and filtering off the fraction of low solubility in water, which was washed with water and dried (fraction A). To the aqueous liquor an equal volume of alcohol was added, and a white solid precipitated, which was filtered off, washed by suspension in hot alcohol several times, and dried at room temperature (fraction B).

The properties of these two substances were found to be as follows:

Fraction A. This is only slightly soluble in water but more soluble in alcohol; it is stable to heating to over 250° C, and soluble unchanged in concentrated sulphuric acid Analysis: N (Kjeldahl), 32·0 per cent; P, trace. The general properties agree with those for cyanuric acid $(CNOH)_3$ (theoretical $N \doteq 32{\cdot}5$ per cent.)

0 1 g. dissolved in 3 ml. water plus 6 drops of ammonia gave, on the addition of copper sulphate solution, a precipitate consisting of microscopic

amethyst crystals, stated by Mulliken ("Identification of Pure Organic Compounds," Vol. II, p. 84) to be characteristic of cyanuric acid.

It is concluded that fraction A is cyanuric acid.

Fraction B. This took the form of a white granular powder, readily soluble in water, but insoluble in alcohol. Analysis: Total N (Kjeldahl), 14·9 per cent.; P, 30·9 per cent. A 5 per cent. aqueous solution has a *pH* 6·7.

Ammonia is liberated on treatment with cold sodium hydroxide solution or on warming with magnesium oxide and water, the ammonia yield on distillation from 5 per cent. sodium carbonate solution is 12·8 per cent. calculated as N_2; the aqueous solution gives a white precipitate with silver nitrate solution, and a white precipitate with cadmium chloride in acetic acid. The material is therefore almost certainly an ammonium salt, and reacts as a pyrophosphate, not as an orthophosphate. Di-ammonium pyrophosphate, $(NH_4)_2H_2P_2O_7$, contains theoretically 13·2 per cent. nitrogen, and 29·3 per cent. phosphorus.

The yield of ammonia from fraction B does not account for the whole of the nitrogen content found, there is a residual 2·1 per cent. nitrogen. It is concluded that the fraction B is di-ammonium pyrophosphate with nitrogenous impurity, probably unchanged urea or biuret.

Fractions A and B together constituted over 95 per cent. of the reaction product so that other substances could be present only in insignificant amounts. In particular, there was no evidence of formation of amidophosphoric acids, or of complex polymers.

The summarised equation:

$$CO(NH_2)_2 + 2H_3PO_4 = (NH_4)_2H_2P_2O_7 + CO_2$$

requires 1·23 g. of urea for 5 g. of 80 per cent. phosphoric acid so that in the above preparations (Section 9 (iii)) there was considerable excess of urea. The results in Table VI showed, as noted above, that the nitrogen not recoverable as ammonia fell to zero when 2 g. of urea were used with 5 g. of 80 per cent. phosphoric acid. On adding an equal volume of alcohol to such a mixture a viscous liquid settled out, which, after separation and treatment with a further quantity of alcohol, formed a granular solid containing 12·0 per cent. nitrogen and 29·7 per cent. phosphorus, and which yielded 14·4 per cent. ammonia (calculated as NH_3) on distillation from 5 per cent. sodium carbonate solution.

This appeared to be di-ammonium pyrophosphate virtually free from nitrogenous impurity.

10. Examination of Water Washings from Cured Fabric

Fabric was impregnated with a liquor containing 100 g. of urea and 50 g. of 75 per cent. phosphoric acid heated momentarily to 180° C. and then cooled and diluted with 92 ml. of water. The cure was for 15 minutes at 170° C.

The cured fabric was washed in water at 70° C. for 15 minutes, and the wash water retained. Further similar washes with water were given, and part of the fabric was also washed in 0·5 per cent. sodium hydroxide solution for 15 minutes at 70° C.

The first wash water was concentrated *in vacuo* and three solid fractions were obtained therefrom:

(*a*) Material slightly soluble in water, containing 37·9 per cent. nitrogen and 1·3 per cent. phosphorus, and giving the cyanuric acid reactions. Apparently it was impure cyanuric acid.

(*b*) Material soluble in water precipitated by alcohol as a paste, containing 28 per cent. phosphorus and 13·5 per cent. nitrogen, and giving the reactions of an ammonium salt and a pyrophosphate; this apparently was di-ammonium pyrophosphate.

(*c*) A substance extremely soluble in water, not precipitated by alcohol, containing 40·5 per cent nitrogen, and 3·0 per cent. phosphorus and giving the reactions of both urea and biuret; apparently it was a mixture of these two substances contaminated with phosphoric acid.

The second wash water yielded only a small amount of material precipitated by alcohol, containing 27·1 per cent. phosphorus and 11·9 per cent. nitrogen There was insufficient for more precise identification, but this material was probably impure ammonium pyrophosphate

The third and fourth washes yielded nothing in significant amount.

During the washing with sodium hydroxide the odour of ammonia was detected. No other identifiable constituent was found.

The soluble matter removed by water after curing the fabric thus appears to be the same as is formed on heating urea and phosphoric acid in bulk in the absence of cellulose, *i.e.* ammonium pyrophosphate, cyanuric acid, urea and biuret.

11. Attempts to Flameproof Fabrics using Phosphates

Since it appeared probable from the experiments recorded under 9 and 10 that di-ammonium pyrophosphate was the active fireproofing agent, the effect on fabrics of this and other phosphates was tried.

Except where otherwise stated, fabrics were padded so that they retained about 5 per cent phosphorus; they were then dried and cured at 165° C. for 10 minutes. They were washed in water at 70° C for 15 minutes, dried and tested for flameproofness. Where any degree of flameproofness was found, phosphorus and total nitrogen contents were determined.

The three ammonium orthophosphates and sodium pyrophosphate all failed to give flameproofness.

For the trials with ammonium pyrophosphate, solutions were made in the laboratory by two methods·

(*a*) Sodium pyrophosphate in concentrated solution was treated with lead acetate, the precipitated lead salt washed and suspended in water and sulphuretted hydrogen passed in to form lead sulphide, which was filtered off. To the filtrate of pyrophosphoric acid, ammonia was added in amount to correspond to either $(NH_4)_2H_2P_2O_7$ or $(NH_4)_4P_2O_7$, as required.

(*b*) 80 per cent. phosphoric acid was heated to 225° C. until the loss in weight corresponded to the formation of pyrophosphoric acid, which was then diluted and treated with the theoretical quantity of ammonia solution to give the di- or tetra-ammonium salt, as required

Solutions made by both methods gave similar results in practice.

The following were the results obtained with pyrophosphates·

(i) Initial trials with ammonium pyrophosphates showed partial flameproofing and about 1 per cent. retained phosphorus Increasing the amount of pyrophosphate applied did not increase the amount of phosphorus retained after washing to any appreciable extent, and even when the amount of applied solids was over 70 per cent. of the weight of the fabric the phosphorus retained after washing was only 2·2 per cent and the nitrogen 0 92 per cent Varying the *pH* value of the pyrophosphate liquor between 4·5 and 10 showed that phosphorus fixation increased with decrease in *pH* value, but scorching and tendering also increased. Varying the conditions of cure, using a pyrophosphate liquor at *pH* 6, showed no significant rise in phosphorus fixation above 1 per cent.

(ii) Ammonium pyrophosphate liquors containing 4 per cent boric acid or 5 per cent. pyridine as possible catalysts, were no more effective than simple pyrophosphate liquors, and the phosphorus fixed did not exceed 1 per cent.

(iii) A pyrophosphoric acid liquor was adjusted to *pH* 8 with triethanolamine instead of ammonia. After padding, curing and washing there was no apparent flameproofing, and the phosphorus content of the cloth was only 0·15 per cent.

(iv) Cotton cloth was pretreated with 98 per cent. formic acid, and after a roller-nip was padded with ammonium pyrophosphate solution at *pH* 6. After curing and washing in water there was only partial flameproofing, the phosphorus content being 0 55 per cent.

(v) An ammonium pyrophosphate liquor prepared by method (*b*) above was adjusted to *pH* 6, and urea amounting to 15 per cent of the weight of the fabric was added. After padding, curing and washing, the dried fabric was almost completely flameproof, and contained 2·4 per cent phosphorus and 1·1 per cent. nitrogen. When this trial was repeated adding cyanuric acid instead of urea, there was only partial flameproofing and the fabric contained 0·52 per cent. phosphorus and 0·47 per cent. nitrogen.

(vi) An ammonium pyrophosphate was prepared by heating 2 g. of urea and 5 g. of phosphoric acid to 170° C. to a clear glassy solid, dissolving the latter in water and precipitating the solution with alcohol A solution of this was padded on to a cloth and cured; after washing there was only partial flameproofing, and the amount of phosphorus fixed was 1·1 per cent

(vii) An ammonium pyrophosphate identical with fraction B described in Section 9, that is containing nitrogenous impurity, was padded on to cotton cloth, which was then cured, washed, and dried. The treated cloth was almost completely flameproof, and contained 2·6 per cent. of fixed phosphorus.

12. Measurement of Increase in Weight in relation to Phosphorus Content of Fabrics treated with Urea-Phosphoric Acid

Cotton fabric was impregnated with a solution of urea-phosphoric acid, prepared by heating 200 g. of urea and 100 g. of 75 per cent. phosphoric acid to 180° C. cooling and diluting with 170 ml. of water, and 14 ml of 28 per cent. ammonia solution. The impregnated fabric was dried and portions were cured at various temperatures for 15 minutes in order to obtain a range of phosphorus contents. All of the portions were given five successive washes in tap water at 60°-65° C. for 10 minutes each wash (except in the case of (*e*) where the fabric was washed in distilled water). A liquor/cloth ratio of approximately 100 · 1 was used in the wash treatments.

(*a*) Four portions of fabric, Nos 1, 2, 3 and 4, representing each temperature of cure, were dried at 105° C for 2 hours, increase in weight, phosphorus content, and yield of ammonia by distilling the fabric from magnesium oxide, were determined. (Distillation from magnesium oxide, was here substituted for distillation with sodium carbonate as being a somewhat more specific estimation of the ammonium radicle) The results are given in Table VII The mean yields of ammonia and phosphorus content correspond to a ratio of 1 gram-atom of phosphorus to 0 85 gram-mols. NH_3.

In three cases out of the four the observed increase in weight is nearer the weight calculated from the phosphorus content for orthophosphate formation than that similarly calculated for pyrophosphate formation. The mean increase in weight is very near to that calculated for orthophosphate formation.

(*b*) Two portions of washed fabric, Nos. 5 and 6, were immersed in 1·75 per cent. hydrochloric acid solution for 1 hour at room temperature and washed thoroughly with water at 60° C. until free from acid. After drying at 105° C. for 2 hours, increase in weight and phosphorus content were determined. The results are shown in Table VIII. The mean increase in weight is very close to that calculated for orthophosphate formation.

(*c*) Portions No. 7-No. 10 of fabric, acid-treated as in (*b*) were immersed in 5 per cent. lead acetate solution for 30 minutes at 70° C. then washed with water until the washings were free from lead. Lead, phosphorus and increase in weight were determined on the samples after drying to constant weight. The results are shown in Table IX. The proportion of phosphorus to lead in gram-atoms corresponds to a ratio of 1 to 1·05.

(*d*) Further portions of fabric (Nos 11 and 12) were immersed without acid-treatment in lead acetate solution at 70° C. for 30 minutes, then washed as in (*c*). Lead, phosphorus, and increase in weight were determined. The results obtained are shown in Table X. The proportion of phosphorus to lead in gram-atoms corresponds to a ratio of 1 to 1·07.

(*e*) Further portions of fabric (Nos. 13-15) were cured, and washed in distilled water at 65° C.; twelve successive washes were given, then the fabric was dried to constant weight Portions of the dried fabric were immersed in N/2 sodium hydroxide solution at 40° C. for 15 minutes, washed in distilled water until the washing water was free from alkali, then dried at 105° C. Phosphorus, sodium and yield of ammonia were determined. The results are shown in Table XI. The ratio of phosphorus to ammonia corresponds to 1 gram-atom of phosphorus to 0·94 gram-mol NH_3, or very nearly 1 to 1. Comparing this ratio with the ratio of 1 to 0 85 found in (13) (*a*) above, it seems that tap water removes more ammonia than does distilled water, no doubt due to cation exchange. The ratio of phosphorus to sodium in gram-atoms is 1 to 1·85, approximately 1 to 2

NOTE.—In the experiments involving fixation of lead and sodium, control samples of unproofed fabric were included to ensure that the washing treatments were effective in removing all unfixed lead or sodium.

13. Method of Assessing Flameproofing Efficiency

After trying various tests which have been proposed for flameproofed fabrics, the test ultimately adopted was to cut a 6-in × 1-in strip of fabric, hang it vertically in a draught-free enclosure and ignite the lower edge with a Bunsen flame. Fabrics adequately treated with urea-phosphoric acid, *i e.* those containing 3 per cent or more phosphorus, charred whilst the Bunsen flame was applied, but ceased to burn or char immediately the Bunsen was withdrawn. These are described as "completely flameproof". Materials containing smaller amounts of phosphorus were found to burn slowly after withdrawal of the Bunsen, but to leave a black ash skeleton retaining fabric structure; these are described as "partially flameproof", and, if necessary, the rate at which they propagate flame after withdrawal of the Bunsen can be estimated in seconds per inch. Untreated cotton fabrics flame immediately; the flaming continues on withdrawal of the Bunsen, and the entire strip is consumed in a few seconds, leaving only a small fragile white ash which smoulders and usually breaks up.

For the purpose of the present work, this test was found preferable to others in which pieces of fabrics are clamped at 45° and subjected to standard flame tests.

IV. CONCLUSIONS

The treatment of cotton fabrics with mixtures of urea and phosphoric acid followed by a "curing" at a temperature of 130°-175° C. gives a flameproof finish which is resistant to hot water washing and even to mild soap scouring The efficiency of the flameproofing has been shown to depend on the phosphorus content of the treated material, and for complete flameproofing a minimum of 3 per cent. of phosphorus is necessary This phosphorus is strongly bound by the cellulose and is not removed even by boiling 1 per cent. caustic soda. It is associated with nitrogen present as the ammonium radicle and easily removed as ammonia by alkali.

Cotton fabrics flameproofed by urea-phosphoric acid lose some of their flameproof properties on repeated washing with alkaline detergents, but the loss of flameproof property is not due to removal of phosphorus, and the original degree of flameproofing can be restored by an acid treatment.

The evidence points to surface esterification of the cotton cellulose as the reason for the flameproofing effect and indicates that the ester present in the washed fabric is the ammonium salt of cellulose orthophosphoric acid, although the products of heating urea and phosphoric acid to curing temperature have been shown to be essentially di-ammonium pyrophosphate and cyanuric acid. The former is no doubt the active esterifying agent.

In the presence of the cellulose the urea does more than just supply ammonia to form the ammonium salt of the acid and so reduce tendering; the excess urea is necessary as a medium to secure an effect which does not seem to be attained in any other way, *i.e* the fixation of about 3 per cent. of phosphorus without great loss of tensile strength.

The work described in this report was commenced in 1945, and has been carried out in the laboratories of the Chief Chemical Inspector, Ministry of Supply. It has previously been the subject of an official Departmental report. The authors wish to thank the Chief Scientist, Ministry of Supply, for permission to publish this present paper.

REFERENCES

[1] Champetier. *Compt. rend.*, 1933, 196, 930.

[2] D R P. 547812 (Cellulose treated with orthophosphoric acid and phosphorus oxychloride for five days)

[3] D.R.P. 556590 (Cellulose treated with orthophosphoric and sulphuric acids)

[4] B.P 279796 (Alkali cellulose treated with phosphorus oxychloride in benzene)

[5] U S.P. 1896725 (Cellulose heated with orthophosphoric acid and acetic, boric and formic acid catalyst).

[6] B.P 183908 (Cellulose dispersed in colloid mill and treated with sulphuric and orthophosphoric acids *in vacuo* at 30-50° C).

[7] B P. 192173 (Alkali cellulose treated with phosphorus oxychloride in inert solvent)

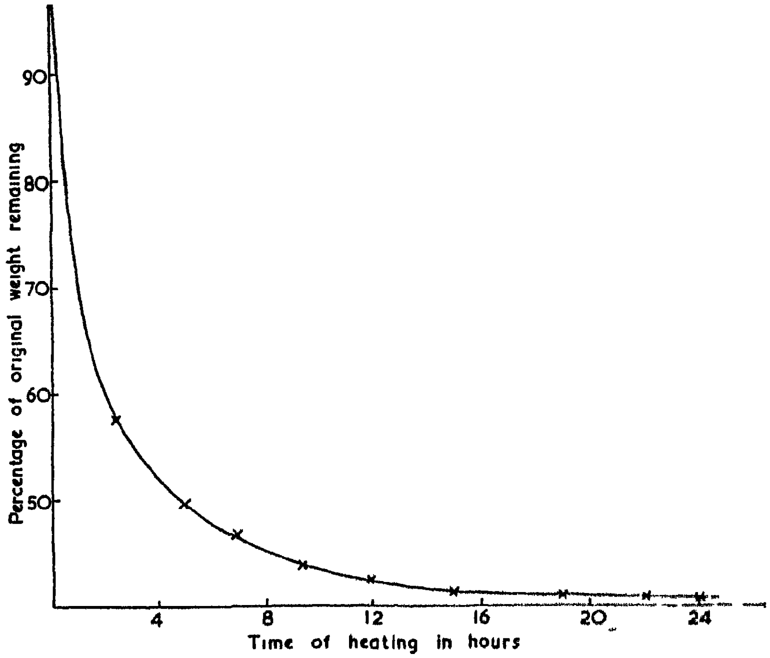
[8] Birtwell, Clibbens and Geake, *J Text Inst*, 1926, 17, 145.

[9] A C Neussle, *J S D C*, 1948, 64, 342

[10] Jurgens, Reed, & Guthrie *Textile Research Journal*, 1948, 18, 42-4.

[11] R W Little *Flameproofing Textile Fabrics.*

APPENDIX



Loss in Weight on heating Urea-phosphoric Acid Mixture at 175° C.

Table I

Trials involving simple urea-phosphoric acid impregnants. Effect of variations in impregnant and cure on fixation and loss in strength

(Section III 2)

Urea-acid Ratio	Type of Liquor	Time of Cure (mins)	Temperature of Cure ° C	Phosphorus Content %	Total Nitrogen Content %	Loss in Strength % of original	Flame-proofing
2 7 1	Neutral	15	150	3·8	1·7	20	Partial
,,	,,	30	147	3·9	2·0	28	Complete
,,	,,	60	145	4·3	2·2	36	,,
1.1	,,	5	146	4·1	1·7	24	,,
,,	,,	15	150	4·9	1·8	31	,,
,,	,,	30	150	4·7	2·0	34	,,
2 7 1	Acid	5	146	4·7	1·6	27	,,
,,	,,	15	150	5·1	2·2	27	,,
,,	,,	30	148	5·1	2·3	30	,,
1.1	,,	5	149	4·5	1·6	40	,,
,,	,,	15	152	4·8	1·8	46	,,
,,	,,	30	150	5·5	1·9	49	,,

Table II

Trials involving liquor with treated formaldehyde. Effect of variations in cure on fixation and loss in strength

(Section III 3)

Time of Cure (min.)	Temp. of Cure °C.	Phosphorus Content %	Nitrogen Content %	Loss in Strength % of original	Flame proofing
120	130	3·95	4·41	17	Complete
60	130	3·47	3·36	19	,,
30	130	2·55	1·87	16	,,
60	137	3·92	4·16	18	,,
30	137	2·58	2·01	17	,,
30	145	3·40	3·04	19	,,
15	160	3·96	3·11	23	,,
10	175	4·30	2·98	29	,,

Table III

Trials involving impregnant treated with formaldehyde. Effect of scouring on nitrogen and phosphorus contents : Series I

(Section III.4)

Time of Cure (mins.)	Temp. of Cure °C.	Washing Treatment	Phosphorus Content %	Total Nitrogen Content %	Loss in Strength % of original
20	145	Water at 55° C. for 15 mins ...	3·4	3·15	17
20	145	Soap/Na_2CO_3@ 80° C for 30 mins.	3·2	0·82	8·2
8	175	Water @ 55° C. for 15 mins .	4·2	2·50	27
8	175	Soap/Na_2CO_3 @ 80° C. for 30 mins	4·1	0·61	12

Table IV

Trials involving impregnant modified with formaldehyde. Effect of scouring on nitrogen and phosphorus contents : Series II

(Section III 5)

Treatment	Phosphorus Content %	Ammonia Content %	Total Nitrogen Content %
Cured only .	5·66	4·0	11·1
One water wash at 70° C for 15 mins	5·25	2·8	3·27
Scour in 0·5% Soap and 0·2% Soda at 70° C for 30 mins ..	4·24	0·7	0·9
Six successive water washes at 70° C.	3·98	1·9	1·8
Boiled in 1% NaOH for 30 mins	3·19	nil	0·1
Boiled in 1% $Ba(OH)_2$ for 30 mins.	3·66	nil	0·1

Table V

Effect of scouring on patterns processed by Patentees

(Section III 6)

Treatment	Phosphorus %						Total Nitrogen %					
	Cloth No						Cloth No					
	1	2	3	4	5	6	1	2	3	4	5	6
As received .	3·3	3·3	3·2	3·0	3·3	3·6	6·3	6·6	7·9	5·7	7·0	5·5
Boiling water 30 mins	3·1	3·2	2·9	2·7	3·2	3·3	5·1	5·2	4·7	4·1	5·2	4·9
Soap scour 30 mins at 70° C	3·1	3·2	3·0	2·8	3·1	3·2	3·2	3·5	3·4	2·5	3·5	3·2
4 Scours as above . ..	3·1	—	—	2·6	—	3·2	1·0	—	—	0·9	—	1·2
10 ,, ,, ,,	3·1	—	—	2·7	—	3·1	0·65	—	—	0·6	—	0·6
Soap scour 30 mins at 94° C	3·1	—	—	2·7	—	3·2	2·4	—	—	2·4	—	3·3
4 Scours at 94° C	2·9	—	—	2·6	—	3·0	0·75	—	—	0·75	—	0·8
Boiling 0·5% NaOH, 30 mins. ...	3·3	—	—	2·9	—	3·4	0·4	—	—	0·3	—	0·4

Table VI

Effect of heating various amounts of urea with 5 g. phosphoric acid at 175° C. for 8 hours

(Section III.9)

Test No	Grams Urea to 5 g 80% H_3PO_4	Final Weight (g)	Loss in Weight (g)	Total N_2 (g.)	Yield of Ammonia (g)	Nitrogen not yielding NH_3 (g)	Total phosphorus (g)
1	24	13 15	15·8	4·50	1·04	3 64	1 33
2	18	9 5	13 5	3·17	0·78	2 54	1 49
3	16	9 2	11·8	2 52	0·79	1 87	1·30
4	12	7·5	9 5	2 43	0 72	1·61	1·36
5	10	6 35	8 65	1·58	0·70	1·00	1·24
6	6	5 25	5 9	1·04	0 72	0·45	1·16
7	4	4 45	4·55	0·74	0·69	0 17	1·40
8	2	4 20	2 8	0·57	0 69	Nil	1 32
9	1	4 40	1 6	0 47	0·56	0·007	1·48

Table VII

Increase in weight of fabrics impregnated with urea-phosphoric acid mixture and cured

(Section III 12*a*). (All figures are in ounces per sq yard of fabric)

	Fabric No. 1	Fabric No 2	Fabric No 3	Fabric No 4	Mean Value
Weight of original fabric	6 5	6 5	6 5	6 5	6 5
Weight of cured and washed fabric .	7 13	7 12	7·62	7 53	7 35
Increase	0·63	0·62	1·12	1 03	0 85
Phosphorus expressed as P_2 .. .	0·203	0·205	0·341	0 370	0 280
Ammonia expressed as NH_3 .	0·094	0·103	0 159	0 164	0 130
Phosphorus expressed as PO_3NH_4	0 635	0·642	1·070	1 160	0 877
Ammonia expressed as PO_3NH_4	0 535	0 586	0 906	0 937	0 741
Phosphorus expressed as $P_2O_5(NH_4)_2$ minus 2H . .	0 577	0 582	0 970	1 040	0 792
Ammonia expressed as $P_2O_5(NH_4)_2$ minus 2H . .	0 486	0 533	0 823	0 848	0 768

Note —Phosphorus and nitrogen would be added as PO_3NH_4 if a cellulose orthophosphate ester were formed, or as $P_2O_5(NH_4)_2$ minus 2H if a pyrophosphate ester were formed.

Table VIII

Increase in weight of fabric impregnated with urea-phosphoric acid cured and acid-treated

(Section III 12*b*) (All figures are in ounces per sq yard of fabric)

	Fabric No 5	Fabric No 6	Mean Value
Weight of original fabric	6 5	6 5	6 5
Weight after curing, washing and acid treatment ...	6 71	7·28	6 995
Increase	0·21	0·78	0·495
Phosphorus expressed as P_2	0·107	0·279	0·193
Phosphorus expressed as PO_3H	0·276	0·720	0 498
Phosphorus expressed as P_2O_5 . .	0·245	0·640	0 443

Table IX

Increase in weight of fabric impregnated with urea-phosphoric acid, cured, acid treated, and lead treated

(Section III. 12*c*) (All figures are in ounces per sq yard of fabric)

	Fabric No. 7	Fabric No 8	Fabric No 9	Fabric No 10	Mean Value
Weight of original fabric .	6 5	6 5	6 5	6·5	6 5
Weight of lead-treated fabric . .	7 46	8 13	8 50	9·47	8 39
Increase	0 96	1 63	2 00	2 97	1 89
Phosphorus expressed as P_2 .	0 093	0·196	0·196	0 300	0 196
Lead expressed as Pb .	0 669	1 362	1·388	2·096	1 376
Phosphorus expressed as PO_3Pb minus H	0 850	1·802	1 802	2 760	1 804
Lead expressed as PO_3Pb minus H . .	0·921	1 875	1 912	2·886	1 899

As the molecular ratio of phosphorus to lead is approximately 1 1 the lead cannot be present in a pyrophosphate grouping For that reason phosphorus and lead expressed as P_2O_5Pb minus 2H are not shown.

Table X

Increase in weight of fabric impregnated with urea-phosphoric acid, cured and lead treated

(Section III 12*d*). (All figures are in ounces per sq. yard of fabric)

	Fabric No. 11	Fabric No 12	Mean Value
Weight of original fabric	6 5	6 5	6·5
Weight of lead-treated fabrics	9·31	10·43	9 87
Increase	2 81	3 93	3·37
Phosphorus expressed as P_2 . . .	0 301	0·409	0·355
Lead expressed as Pb	1 875	2 870	2·373
Phosphorus expressed as PO_3Pb minus H	2 770	3 760	3·265
Lead expressed as PO_3Pb minus H	2 580	3 950	3·265

Table XI

Analysis of fabrics impregnated with urea-phosphoric acid, cured, caustic soda treated.

(Section III. 12*e*)

	Fabric No 13	Fabric No 14	Fabric No 15	Mean Value
Phosphorus expressed as P_2% . . .	3 64	3 73	2 93	3·43
Sodium expressed as Na % ...	4·79	4 94	4·40	4 71
Ammonia displaced expressed as NH_3 %	1 93	1 85	—	1 89
Ratio NH_3 P	0 97	0·90	—	0 935
Ratio Na . P	1 79	1 77	2 00	1 85

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53—REGENERATED KERATIN FIBRES FROM WOOL

By F. Happey and R L Wormell

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SUMMARY

A description is given of methods of dispersion of wool and its extrusion into continuous filament yarn with a β keratin structure The soluble protein curd is made by extraction with sodium sulphide This product is precipitated, redissolved and refined in cuprammonium solution and then reprecipitated A final solution of approximately 35 per cent. concentration is made from the wet curd with either ammonia or cuprammonium and after filtration, the yarn is spun into a salt bath and prehardened The yarn is then stretched and hardened in two stages, the final product has a tenacity of about 1 gm. per denier and an extension of 30 per cent (approximately) when tested at 65 per cent R.H 70° F

Load/extension curves of the filaments are plotted during various stages of manufacture and these show the improvement obtained in the yarn properties during processing X-ray photographs demonstrate also that with stretching there is an increase in the crystallinity of the β keratin which can be carried almost to the limit by the stretching in steam of the finished yarns In the X-ray photograph of steam stretched regenerated β keratin, there is no obvious spreading of the (hkl) spacings along the hyperbolæ of the fibre diagram when $l \neq 0$, as is the case in wool stretched 100 per cent in steam.

It is suggested that in the work described, there is the basis of a process for the regeneration of a continuous filament β keratin yarn from the α keratin protein of wool This may not appear an attractive proposition from an economic point of view using best grade wools as starting material, but there is no reason why such a method should not be extended to the waste products of the wool trade and to other proteins with an α keratin structure such as horn, hooves, nails and whalebone, *etc*

INTRODUCTION

The general pattern of the methods of wet spinning necessary to produce continuous filaments from solution is now well established, and considerable progress has been made in its application to the regeneration of the known fibrous protein molecules Reference has been made in a preliminary paper[1] to the work carried out with varying degrees of success in the regeneration of casein,[2] groundnut proteins,[3] chicken feather keratin[4] and silk[5] The problem of the reconstitution of wool fibres has, in the past, been considered to be of a more difficult nature mainly on account of the proportionately large number of cystine cross-links which require to be broken down before complete solution can be achieved This dispersion process necessarily causes some degradation of the protein to take place during the isolation and solution of the individual polypeptide chains, thus inhibiting to some extent the step of fibre formation during the extrusion of the filaments Several wool solvents[6] have been described, but the most practical agent for this purpose is probably sodium sulphide[7,8] and one of us (R L W) has described earlier a method of solution of wool keratin[7] which has been applied successfully in the spinning of a mixed polymer from casein and the soluble wool curd This work has now been extended and a simple method of regeneration of wool fibres has been devised Certain features of this process are described in the following and a study of the physical and chemical properties of the experimental products leads us to believe that there is in the work cited the basis of a process for the regeneration of continuous filament yarn of the β keratin type from wool

EXPERIMENTAL

Preparation of the Crude Solubilised Product from Wool

(*a*) 1 kg of merino wool was digested in a small Pfleiderer in 2 kilos of a 25 per cent solution of sodium sulphide The viscous mass was mixed for 24 hours at a temperature of 25° C The resulting dispersion was diluted with 600 c c of water and the whole was removed from the Pfleiderer and filtered through a monel metal gauze This product was then diluted to a volume of 30 litres and the soluble wool product precipitated at *pH* 4 by the addition of hydrochloric acid. The precipitate was washed until acid free and dried at 50° C

(*b*) In this method the technique adopted for dispersion and precipitation of the wool was similar to that for method (*a*), but a rather weaker solution of sodium sulphide of 8 8 per cent was used Yields in both cases were of the order of 65 per cent

METHOD OF YARN MANUFACTURE

Extraction of a Fraction Soluble in Ammonia or Cuprammonium Hydroxide

100 g. of the crude soluble material prepared by method (*a*) of the former section were soaked in 180 c c of distilled water for 1 hour 70 c c of cuprammonium solution (containing 15 g of copper and 200 g of ammonia per litre) were added Solution was achieved by rolling the mixture in a bottle for about 20 hours at 18° C The cuprammonium solution was then diluted to 3 litres and clarified by continuous passage through a Sharples super centrifuge at 20,000 rev /min The protein was precipitated at room temperature by bringing the clarified extract to *pH* 3 by the addition of 10 N sulphuric acid The precipitate was then washed with distilled water and a curd containing about 35 per cent of protein was recovered by pressing

The Production of a Spinning Dope

Method A

The wet curd was placed in a centrifuge bottle and 5 c c of the cuprammonium solution of the last section were added Dispersion of the protein took place readily After stirring to ensure uniform distribution of the cuprammonium solution through the curd, the dope was centrifuged to remove air and any foreign particles, and a dope of 35 per cent concentration at *pH* 8 was obtained

Method B

A few c c of concentrated ammonia were added to the wet curd and dissolution readily took place The dope was manipulated as described in Method A and a concentration of 35 per cent was obtained in alkaline solution at *pH* 8

Extrusion and Coagulation

The dope was extruded as previously described by one of us (R L W) in the case of a mixture of casein and wool keratin, and coagulated in a salt bath of the following composition

$$\left.\begin{array}{l}150\text{ g } Na_2SO_4\\ 450\text{ g } MgSO_4\,7H_2O\end{array}\right\}\text{ in 1 litre of water}$$

The *pH* of the coagulating solution was adjusted to 8 by the addition of a small quantity of sodium carbonate

Prehardening, Stretching and Final Hardening

The filaments were floated vertically from the spinning jet through the above dense salt solution, wound over a godet, and deposited on the surface of a prehardening bath of the same constitution as that used in coagulation, with the addition of 7·5 g of formaldehyde per litre After prehardening at 20° C. for half an hour, the yarn was stretched and hardened in two stages and finally insolubilised At the first stage the yarn was stretched rapidly about 100-150 per cent in a bath of the following constitution at 90° C.

$$\left.\begin{array}{l}100\text{ g. chloral hydrate}\\ 150\text{ g }Na_2SO_4\\ 400\text{ g }MgSO_4\,7H_2O\end{array}\right\}\text{ per litre.}$$

The yarn was then collected on a reel and further hardened to set the extension in a bath containing

$$\left.\begin{array}{l}7\text{-}9\text{ g }HCHO\\ 380\text{ g }Na_2SO_4\end{array}\right\}\text{ per litre}$$

This first stage stretching process gave rise to a fibre which had a load/extension curve as in Fig 9(a)

The second stage stretching was carried out more slowly after the yarn had been swollen in the above aqueous chloral and salt solution at 50° C -60° C , and the regenerated keratin was finally hardened and insolubilised [2,7] At this stage, an extension of approximately 100 per cent was applied to the fibres After drying and conditioning, the yarn gave a load/extension curve as in Fig 9(b), and an X-ray photograph illustrated in Fig. 5

Testing of Yarns

Load/extension curves of single regenerated wool fibres were plotted using a single filament extensometer with a constant rate of loading of 12 g per minute The results obtained are shown in Figs 9 and 10

In Fig 9, curve A shows the results obtained for a typical regenerated filament taken after the first stretching and hardening process Curve B is the load/extension curve of a regenerated wool fibre after the final hardening and insolubilising In both cases the fibres were conditioned before testing at 65 per cent R H and 70° F The final curve C of this series shows the load/extension curve of the latter fibre tested wet with water Fig 10 shows the hysteresis effects during continuous loading and relaxation in water with the above rate of application and removal of load, *i e* 12 g per minute

X-ray Photographs

The X-ray photographs were obtained in a manner similar to that described previously,[2] and samples of the protein were investigated during various stages of the manufacture from the parent to the regenerated state Relevant photographs of the material have been reproduced and included in the text Fig 4 is an X-ray photograph of the parent curd Fig 5 is an X-ray photograph of the finished yarn giving rise to a load/extension curve as in Fig 9(b) Fig 6 is an X-ray photograph of yarn stretched in steam

General

Fig 1 is a photograph of a typical skein of regenerated wool fibres giving an X-ray photograph of the type shown in Fig 5, and having a load/extension curve measured under standard conditions as in Fig 9(b) Fig 3 is a photomicrograph of the cross section of this yarn, and Fig 2 is that of a longitudinal view of these fibres taken with the same magnification of 300 ×

RESULTS

General Properties of the Finished Yarn

The final yarn illustrated in Fig 1 had the following properties

(*a*) Denier 900/200 filaments (continuous)

(*b*) Straw coloured and lustrous in appearance, had a lofty handle, was warm and had some slight scroop

(*c*) Breaking load of single filaments 1 g /denier (approximately), and about 30 per cent. extension at break Wet with water, the breaking load was 0·3 g /denier with an extension at break of 33 per cent

(*d*) The filaments were mainly slightly flattened and reniform in cross section, but a few isolated filaments showed a cross section with three distinct bulges

Load/Extension Curves and X-ray Photographs

(*a*) The X-ray photograph of the parent merino wool was a typical pattern of α keratin

(*b*) The crude curd extracts from this above material showed X-ray powder diagrams of β keratin (Fig 4)

(*c*) The spun yarn at the prehardening stage, both in this condition and after a further hardening process excluding the stretching stage of the preparation gave an X-ray photograph of a β protein with little or no obvious orientation of the crystallites along the fibre axis In both types of crude curd extracted with either an 8·8 per cent or a 25 per cent sodium sulphide solution, similar β keratin diagrams were obtained by X-rays, but only small relevant differences in the properties of the yarns made from the two parent materials were found

Table I

Showing Tenacities and Extensions at Break of Regenerated Wool Fibres after the First Stage of Stretching and Hardening, made from Curds Extracted with 8·8 per cent and 25 per cent. Sodium Sulphide

Description of Sample	Filament denier	Tenacity g /denier Mean of 15 measurements		Extension Mean of 15 measurements	
		Conditioned at 65% R H 70°F	Wet	Conditioned at 65% R H 70°F	Wet
Keratin fibres spun from 25% sodium sulphide dispersion	7·28	0·47	0·13	9·6%	76%
Keratin fibres spun from 8·8% sodium sulphide dispersion	5·7	0·56	0·17	11%	76%

Typical differences obtained are illustrated in Table I, but it will be shown that these are relatively smaller than might be expected considering the differences in alkalinity of the two extracting solutions The load/extension curve of Fig 9(a) which is for yarn at this stage made from a curd extracted with the 8·8 per cent solution of sodium sulphide has a tenacity of about 0·60 g /denier and approximately 7·5 per cent extension at break after the first hardening stage

(*d*) The effects of stretching, hardening and insolubilising as described earlier are as follows·

(1) The filaments commence to show orientation of the protein chains parallel to the fibre, the structure is still retained as a β keratin configuration, and the backbone spacing of 4·64 Å and the side chain spacing of 10 Å (approximately) are clearly resolved along the equator of the X-ray diagram of the material

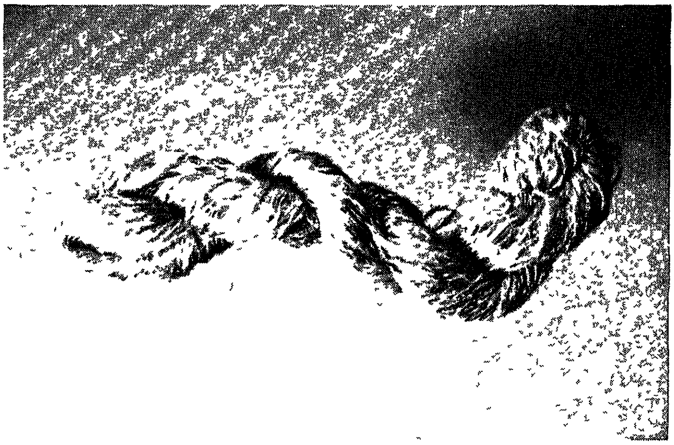

Fig 1

Photograph of 1 oz skein of Untwisted Regenerated Keratin Yarn of 900 denier/200 filaments made from wool The undyed specimen was lustrous, straw coloured and full in handle

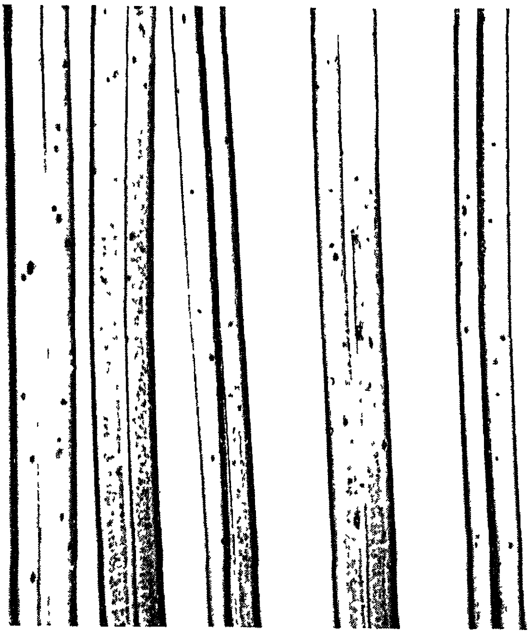

Fig 2

Photomicrograph in longitudinal direction of filaments of Regenerated Wool Fibres Magnification × 300.

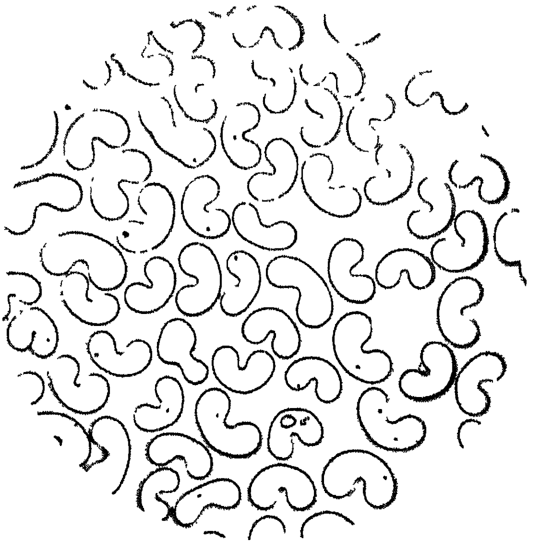

Fig 3
Photomicrograph of cross section of Regenerated Wool Fibres showing the reniform shape of the filaments perpendicular to the fibre axis Magnification × 300

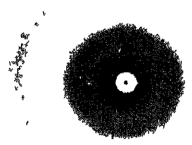

Fig 1
X-ray photograph of Soluble Keratin Curd made from wool fibres showing a typical disorientated β pattern Cu $K\alpha$ radiation D = 4 cm

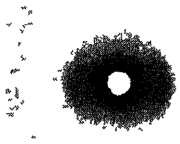

Fig 5

X-ray photograph of Regenerated Wool Fibres made by a stretch spinning process The filaments show a slightly orientated β keratin structure (Fibre axis vertical) Cu Kα radiation D 4 cm

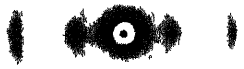

Fig 6

X-ray photograph of highly stretched Regenerated Wool Fibres showing a highly orientated and well developed crystalline β keratin structure (Fibre axis vertical) Cu Kα radiation D 4 cm

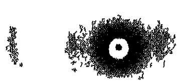

Fig 7
X-ray photograph of highly orientated Casein Fibres showing reflexions from a normal β and cross β protein structure Cu Kα radiation D=4 cm

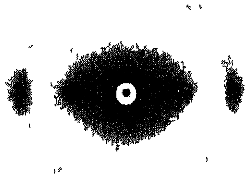

Fig 8
X-ray photograph of Merino Wool stretched in steam 100% of its original length and showing the β keratin structure The reflexions from planes in the zone [001] can be seen to spread along the hyperbolae of the photograph The spreading of these spots is the main dissimilarity between the X-ray photograph of these fibres and that of Regenerated Keratin stretched in steam of Fig 6 Cu Kα radiation D=4 cm

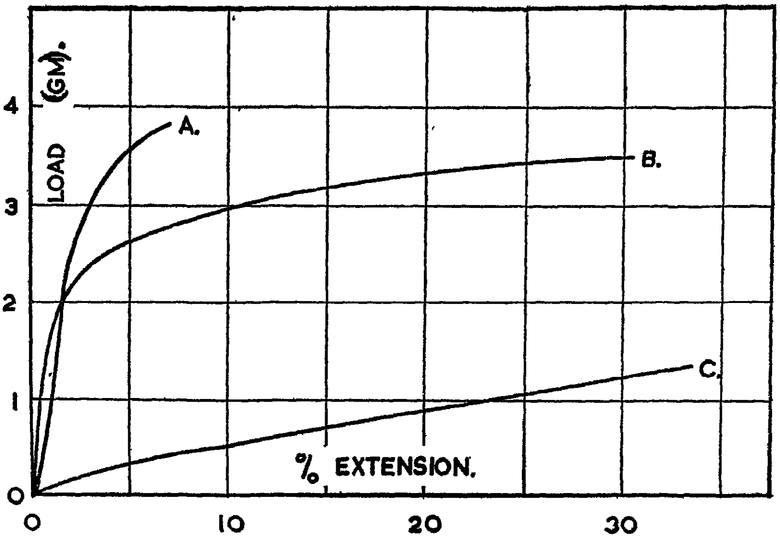

Fig 9

Load/Extension Curves of Regenerated β Keratin Fibres from Wool.

A Load/extension curve of fibre after pre-hardening treatment, measured at 65% R H. 70°F Filament denier 6·37

B Load/extension curve of fibre after stretching and hardening, measured at 65% R H and 70°F Filament denier 3 36

C Load/extension curve of fibre as in B but measured wet with water, Filament denier 3 4

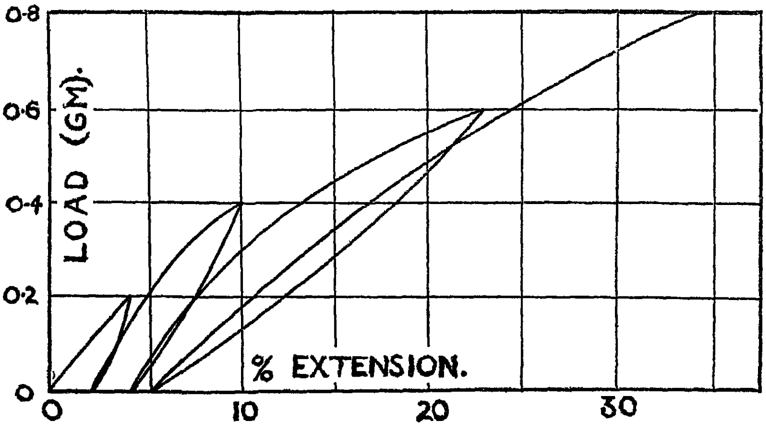

Fig 10

Load/extension Curves of Regenerated Wool Filament (denier 4 0) in water showing hysteresis effects on repeated loading and relaxation Rate of loading 12 grams per minute

The load/extension curve shows considerable changes—the filaments increase in tenacity to about 1 g./denier with an extension at break of 30 per cent. (approximately). Some improvement in the wet tenacity to 0·3 g /denier after the second stage of stretching was found and the extension at break was only slightly greater than in the dry condition. Fig 10 is a series of load/extension curves carried out in water on a fully hardened and insolubilised fibre, and shows that under the conditions of experiment, a considerable amount of spontaneous elastic recovery is present in the fibre.

(2) The fibres described in the last section were extended approximately 40 per cent. in wet steam and the X-ray photograph of the product is shown in Fig. 6. This photograph is one of a highly orientated and crystalline sample of β keratin. Measurements from the X-ray diagrams show that in this case the backbone spacing is 4·55 Å, the side chain spacing is 10 Å (approximately) and the amino acid repeat along the fibre axis is 3·27 Å. The similarity between this photograph and that of wool stretched in steam to 100 per cent. extension is quite clear, but in the latter case the spacings (hkl), when $l \neq 0$, tend to spread along the hyperbolæ of the fibre diagram,[9,10] whereas the spacings in the regenerated wool diagram are comparatively sharp in all cases.

DISCUSSION

The Mechanism of Solution of Keratin

It is generally recognised that the dispersion of wool keratin in sodium sulphide is rendered possible by the breakdown of the cystine cross linkages between the polypeptide chains. Further, it has also been considered that during this rupture of side chains by the alkaline agency, some degradation of the molecular chain length is bound to occur This degradation of the chain length should take place at a greater rate in the case of the highly concentrated sodium sulphide solutions, and some reduction in the acid precipitable fraction of solutions at higher concentrations has already been reported by Breese Jones and Mecham[8] This effect is confirmed to some extent when the physical properties of regenerated keratin fibres are examined; in Table I it can be seen that fibres made from a 25 per cent. sodium sulphide extracted curd are inferior in strength to those made under similar conditions from 8·8 per cent. solutions. Further, the latter material was found easier to work in the processes of fabrication from curd to final fibres than was the former specimen extracted at a higher *pH*. Having made this point of some small differences in the two materials, we feel, however, that this variation in yarn properties is not so great as might have been expected considering the differences in alkalinity of the two extracting solutions Although the hydrolysis of peptide links must be clearly recognised as a concomitant effect of treatment with alkali sulphide, our experiments suggest that this may not be so great as had previously been suspected. One factor which may reduce the rate of hydrolysis of the peptide linkages by the sulphide may be the presence of the dispersed protein itself. This may behave in accord with the "Zwitterion" theory and thus protect to some extent the protein molecules in solution from alkaline degradation.

From an X-ray photograph of this protein curd, it can be seen that the specificity of the α fold has been completely destroyed on solution of the wool after breaking the cystine cross links On recrystallisation by precipitation, the β keratin photograph (Fig. 4) is given by the new product and it is clear that a degeneration* of the α protein configuration of the molecule has occurred This allows crystallisation to take place in the usual fully extended β state of the molecule. Work carried out by Mercer[11] has shown that fibres drawn from his soluble wool proteins gave an α keratin configuration, and a detailed comparison of his work with that of ours on the structure of regenerated wool and casein filaments has led us to the conclusion that the protein component giving rise to the α keratin picture may not have completely degenerated into single chains in solution [12] (*See Note added in proof*)*

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* The word "degenerate" is used to denote a protein molecule in solution which is free from inter or intra molecular attachment of a permanent kind and which can thereby on spinning form, along with similar molecules, a fully extended β protein structure It is suggested that a "denatured system" does not always show such properties, and is more applicable in the case of a molecule which has been deprived of its specific biological properties due to external interference of any kind.

Solution of the Protein Curd in Cuprammonium Solution

The nature of the cuprammonium solution of the crude curd for acid precipitation was found to vary considerably with the method of preparation of the latter material. For example, the product from 25 per cent. sodium sulphide solution required about 70 per cent. of its weight of standard cuprammonium solution for optimum solubility of the final spinning solution With higher proportions of cuprammonium solution, increased copper adsorption occurred on the protein molecules and the final soluble product became increasingly difficult to spin. With the curd prepared from 8·8 per cent sodium sulphide solution, an optimum product was obtained using 160 per cent. of standard cuprammonium Here, however, the yield was less than that obtained with the stronger alkali, but further work is in progress to estimate the best conditions for the extraction process by balancing the yield against the quality of the soluble product.

The curd refined as above by acid precipitation can then be finally dissolved in either cuprammonium or ammonia The latter has been found to give the better results as it produces a fibre which has a paler straw colour than that from the cuprammonium solution.

The Influence of Stretching on the Crystallinity of the Regenerated Wool Fibre

On extrusion of the soluble wool molecules, it is clear that a coherent fibre is produced, but that under the conditions of experiment, these fibres have little or no orientation at this stage They are, however, definitely in the β keratin configuration A further hot stretching process after some preliminary hardening causes orientation of the crystallites parallel to the fibre axis. The load/extension curves of the yarns at these stages clearly show the differences in the structure and orientation Under standard conditions of test, the partially stretched and hardened fibre has a tenacity in the region of 0 60 g./denier and a low extension at break. From the handle of the material, the fibres are also rather harsh and brittle. In the wet state at room temperature, the unstretched fibres are highly plastic and can be extended as much as 75 per cent before breaking (see Table I) In this case, the fibres had been only partially hardened and insolubilised; the plastic flow so obtained was probably due to orientation of the crystallites parallel to the fibre axis.

On finally stretching, hardening and insolubilising, the regenerated wool fibres still in the β configuration show orientation of the crystallites parallel to the fibre axis. From the load/extension curves it can be seen that the tenacity under standard conditions of test is in the region of 1 g /denier and the extension is greater than 30 per cent The filament denier is in the region of 4, and from Fig. 9(c), it can be seen that the wet tenacity of the yarn is about 0·3 g./denier. These figures are of the same order as those for casein and vegetable protein filaments at present. In the case of the incompletely finished yarns of Table I, the wet filaments were capable of very high degrees of stretch, but in some of the above samples of yarn, the wet extension was only slightly greater than that of the fibre under normal conditions of test. Fig. 10 is a series of load/extension relaxation curves, and it can be seen that the wet fibres exhibit a considerable degree of immediate elastic recovery on stretching. The recovery curves of a fibre after a series of hysteresis cycles of loading and relaxation show that a fibre stretched 23 per cent. recovers instantaneously on uniform deloading 15 per cent. of its original length. If the fibre is left unloaded, it eventually recovers almost to its original length.

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* *Note added in proof*—Since this paper was written, it has been shown that certain polypeptide molecules when spun or precipitated from solution, may fold into stable configurations which appear similar to α keratin[13] Further, it has also been demonstrated that the copolymer of DL β phenylalanine and glutamic γ methyl ester may be spun in two forms α_{II} and β from the solvents *m*-cresol and formic acid respectively[14]. It is therefore reasonable to conclude that the configuration of the polypeptide is decisively influenced by the solvent from which it is precipitated It is possible, therefore, that Mercer's results may be explained in part along these lines, but in our more recent work on keratin, we have been unable to identify an α structure in the regenerated wool fibre after orientation

Filament Coagulation

The conditions which obtain during the extrusion of filaments have a great influence on the physical characteristics of the final yarn, and this is particularly so in the case of the regenerated wool fibres. Use of a coagulating bath of low *pH* appears to give rise to weak and brittle fibres which are not easily manipulated in the flotation method of spinning. With neutral or distinctly alkaline media for this purpose, good spinning is obtained; in the latter case the rate of precipitation of the protein from solution is probably slower, thus materially assisting in the recrystallisation of the molecules in the initial stages of extrusion. The optimum temperature of this coagulation bath is between 50 and 60° C.

During the spinning of protein, it was found that the best yarns were obtained from dopes of concentration as high as possible consistent with their manipulation at the centrifuging and extrusion stages of preparation. This concentration was found to be particularly high, *i.e.* 35 per cent., in the case of the regenerated wools, probably due to the comparative shortness of the molecular chains and their highly dispersed state in solution

It can be seen that with our present conditions of spinning a filament of comparatively round cross section has not been obtained, and it is most probable that the reniform section (see Fig. 3) is mainly due to the conditions of coagulation If, however, the development of these fibres proceeds similarly to that of other protein fibres, *i.e.* casein, a filament of approximately cylindrical shape should not be difficult to produce

From the experiments already carried out it would appear that the low sulphide curd gives a better fibre than does the high sulphide product. This is clearly obvious in the first stages of spinning from Table I, and the final yarn, as far as can be ascertained at the moment, is of higher tenacity in the former case.

Comparison of Regenerated Wool and Casein Fibres

It has been pointed out in the previous section that the protein content of a regenerated wool dope is about 35 per cent., whereas in casein this concentration is of the order of 20 per cent. The final yarns made from these two materials have in general about the same tenacities and extensions Fig. 7 shows an X-ray photograph of highly orientated casein fibres and here it can be seen that along with the normal β protein diagram there are arcs typical of a cross β configuration. Thus in comparing the physical properties of these two yarns, it is probable that the development of orientation and crystallinity along with variations in molecular weight should be considered.

(*a*) A regenerated wool filament has its crystalline phase as a single component system, *i e.* β keratin, but its chain length is most probably comparatively short.

(*b*) Casein molecules are not fully opened up during solution and probably retain some original specific structure during processing, the molecular weight of the particles is, however, large compared with that of the regenerated wool molecule Further, it is clear that crystallites containing a cross β configuration of the protein molecules are likely to be less elongated along the fibre axis than are those containing only molecules in the fully extended state.

From consideration of this work it is felt that the protein molecules in casein tend to spin more as large elongated globules, which themselves are readily orientated parallel to the fibre axis In support of this suggestion the X-ray diagrams of casein fibres, even of the comparatively disorientated Fibrolane A type show a definite low angle X-ray pattern typical of such a system [2]

Only when additional extension is applied to the casein fibres causing further unfolding of the molecular chains of the globules does the yarn give an X-ray photograph of an orientated protein (Fig. 7). Even under these conditions a single phase system of the crystalline part is not obtained, since clear evidence of the cross β structure is present in the diagram. From this it would appear that contrary to previous suggestions, the process of solution and spinning of casein and peanut protein is not that of single denatured molecules in solution, but there is a possibility that the globular proteins may be only partially opened up, thus retaining in some cases their specific structures. Even under the most drastic conditions of spinning and stretching as at present applied in production, the molecules are not wholly aligned as extended protein chains along the fibre axis.

In the case of the regenerated wool molecules, there is little doubt that the mean chain length is considerably shorter than in casein Thus potentially the wool molecule in solution should not be capable of producing as good a solution as casein from a spinning point of view, provided the latter molecules can be regenerated as an orientated structure containing only a single β protein phase of a fully degenerate system.* On the other hand the regenerated wool molecule is capable of forming this single phase β keratin configuration as can be seen from Fig. 6, and thus from this point of view it is felt that such a highly crystalline protein, even of comparatively short chain length, should give a satisfactory textile yarn.

The Structure of the β Keratin of Native and Regenerated Wool Stretched in Steam

A comparison of Figs 6 and 8 shows that there are detailed differences in the structure of the β keratin of native wool stretched in steam 100 per cent and regenerated β keratin fibres stretched in steam In the former case the reflexions from planes (hkl) when $l \neq 0$, tend to spread along the hyperbolæ of the fibre diagram of Fig. 8 There is, in particular, a spread of the "side chain spacing" of 10 Å (approximately) and also of the (111) spacing along the first hyperbola In the zone [001], however, this definition is not obviously impaired and the backbone spacing (200) of 4·65 Å and the (210) spacing of 3·75 Å are both unchanged and sharp Thus it can be seen that the process of setting of steam of the β keratin structure in wool is accompanied by a considerable distortion of the crystalline lattice in the direction of the side chain spacing

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* See page T864

In the regenerated β keratin fibres, this lattice distortion is not so obv as there is no spreading of the spots clearly visible along the hyperbola of t X-ray diagram of the regenerated yarn stretched in steam. Thus in the s chain direction, the regenerated fibres seem to have crystallised better fr solution than did the native wool molecule on transformation from the α the β form, and with the subsequent "permanent setting" of the β for It is, therefore, likely that an obviously crystalline structure produced b steam in the stretched regenerated wool should most probably produce comparatively strong and stable β keratin fibre when the reactivity of th side chains has first been reduced by crystallisation, and secondly by furth cross-linkage by the usual methods

CONCLUSIONS

The work described in the present paper shows that it is now possible regenerate from the α keratin of wool continuous filament yarn with physic properties comparable with those already obtained for casein. From th point of view, therefore, these orientated β keratin fibres are within the rang of usable textile materials. Further, it is here shown that stretching in stea gives a more highly orientated and crystalline structure in these fibres comparable with those produced in regenerated specimens from chicken feath and egg albumin by Lundgren and his co-workers.[4] In general, it can be sai that dispersed proteins are not readily regenerated into orientated crystallin structures. Howitt and Coleman state that their regenerated silk fibroin gav X-ray powder diagrams in films and little orientation in fibrils. It has al been with some difficulty that we have produced an orientated casein ya The latter problem was, however, complicated by the existence of a cr β structure which tended to mask the effect of the alignment of the crystallit along the fibre axis. During the present series of experiments, only sh lengths of yarn have been submitted to stretching in steam, and in conseque load/extension curves have not, as yet, been obtained. We feel, howev that it should be possible to introduce this additional step leading to production of highly orientated continuous filament yarns with tenacities excess of those quoted in this paper.

In the present process of regeneration of keratin fibres, the extraction efficiency (ratio of fibre yield to original wool by weight) is of the order of 35 per cent., and for this and other reasons it is not likely that virgin wool would form an economic starting material for this process. Comparing th extraction rate with that for the soluble wool curd used in the mixed polymer spinning of wool and casein, it is clear that the latter is a more attractive proposition from the point of view of extraction efficiency. Certain structural problems, of which orientation is one, arise in the case of the mixed proteins, and cause difficulties which will be discussed in detail at a later date

The most pertinent feature of this research with regard to the paren materials is that α keratin need not necessarily be used in the form of go wool. Any waste products of the industry can be treated in the described, as could also the shoddy materials of the rag trade. Then however, a further copious and inexpensive source of supply of raw mate which might be explored in the α keratin of horn, hooves, whalebone, *etc.* In the offal industry these materials are stripped of fats and gelatin, *etc.* leaving, in the main, the insoluble α keratin. It is clear, therefore, that further extraction of this residual α keratin could be carried out to produce a soluble curd, which could be refined and spun into a continuous β ker yarn.

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REFERENCES

[1] R. L. Wormell and F Happey *Nature*, 1949, 163, 18.

[2] F. Happey and R. L. Wormell. *J Soc Dyers and Colourists Symposium on Fibrous Proteins*, 160, May, 1946.
G. Diamond and R. L. Wormell. *J Text. Inst*, 1939, 30, P224

[3] D. Traill. *Chem and Ind*, 1945, 8, 58.
A C Chibnall, K Bailey and W T Astbury. B P. 467,704.

[4] W. H. Ward, L. M High and H. P Lundgren *J. Polymer Res*, 1948, 1, 22.

[5] F O Howitt and D Coleman *Proc. Roy Soc*, A, 1947, 190, 145.
F. O. Howitt and D. Coleman *J Soc Dyers and Colourists Symposium on Fibrous Proteins*, 160, May, 1946.

[6] C Breese Jones and D. K Mecham *Arch. Biochem*, 1943, 2, 193.

[7] R. L. Wormell *J. Text Inst*, 1948, 39, T219

[8] C. Breese Jones and D K. Mecham *Arch Biochem*, 1943, 2, 209.

[9] F. Happey. Ph D Thesis, Leeds (1932)

[10] W. T. Astbury and H. J Woods. *Phil Trans. Roy. Soc.*, A, 1933, 232, 333.

[11] E. Mercer. *Nature*, 1949, 163, 18

[12] F Happey. *Nature*, 1949, 164, 184.

[13] C. H. Bamford, W. E Hanby and F Happey, *Nature*, 1949, 164, 138

[14] C. H. Bamford, W. E Hanby and F. Happey, *Nature*, 1949, 164, 751.

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CORRECTION

Some Observations on the Influence of Fabric Structure on Felting ”

J. Textile Inst., 1949, 40, T734

The captions were inadvertently omitted from the diagram on p. T734. The argument is quite clear from the text, but the left-hand block of four symbols should have been headed “unfavourable to felting”, and the right-hand block “favourable to felting”.

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